ETHYLENE DIBROMIDE

"ROBUST SUMMARIES"

For

BIODEGRADATION and ENVIRONMENTAL FATE

PREPARED FOR
THE GREAT LAKES CHEMICAL CORPORATION

SUBMITTED BY:
HEALTH & ENVIRONMENTAL HORIZONS, Ltd.

DATE: December 5, 2001

CAS#106-93-4 Ethylene Dibromide

A. ENVIRONMENTAL FATE/BIODEGRADATION:

1. REPORT NUMBER: PH-1

STUDY TYPE: Photohydrolysis; effects of irradiation on Hydrolysis

STUDY TITLE: Photohydrolysis of Ethylene Dibromide

AUTHORS: Charles E Castro and Nao O. Belser

DATE of REPORT: Not given

PUBLISHED: The study was published in the Journal of Agricultural and Food Chemistry, 1988, 33, 536.

TESTING FACILITY: Department of Nematology, University of California, Riverside, California 92521.

DATES OF EXPERIMENTAL WORK: Not given.

STUDY NUMBER: No study number or project number were given in the report.

SPONSOR: Department of Nematology, University of California, Riverside, California 92521 and in part by USDA Grant No. 80-CRSR-2-0512, WRIAP Project No.63 .

STUDY OBJECTIVES: The objective of the study was to determine the effect of irradiation on the rate of hydrolysis.

RECOGNIZED METHOD: The authors did not indicate they followed a pre-established protocol or guideline. The reference OECD guideline is OECD 111.

GLP: Pre-GLP.

TEST SUBSTANCE: Ethylene Dibromide (EDB) was obtained from Matheson, Coleman and Bell and was used without further purification

Purity: Purity of the starting material was not given it the report. The substance did exhibit a single peak upon gas chromatography and showed correct mass spectrum.

OTHER MATERIALS: Ethylene oxide was obtained from Matheson, and analytical grade ethylene glycol was obtained from Mallenckrodt and employed without further purification. Bromoethanol was obtained from Eastman Kodak white label and distilled (bp 55-56°C (20 mm)) before use. All substances exhibited a single peak upon gas chromatography and showed correct mass spectra. Potassium ferrioxalate was prepared according to procedure of Parker (1). Water was deionized and glass distilled.

CONTROLS: As an non-irradiated control, Br^- was determined in a 1.0×10^{-3} M solution of EDB that had been standing in a sealed flask for 0.77 year. The concentration of Br^- was 3.2×10^{-4}M. This corresponds to a $t_{1/2}$ of 16 years.

CONCENTRATIONS OF TEST SUBSTANCES: Starting concentrations for all substrates were stated to be in the range of 9.0×10^{-3} to 1.0×10^{-2} M. The study did not state how the concentrations of the starting material were determined.

EXPOSURE PERIOD: Exposure to irradiation varied depending upon the compound being irradiated. EDB: 2hr.; bromoethanol: 3hr.; ethylene oxide: 3 hr.; and potassium ferrioxalate: 15 minutes.

EQUIPMENT: A 700 mL tube-shaped reactor was fitted with serum-capped stopcocks for gas and solution removal, manometer, and magnetic stirring bar. The light well was a concentric, water-jacketed quartz finger. Solution levels were 2-3 cm above the top of the tubular 450-W Hanovia medium-pressure mercury lamp.

TEST PROCEDURE: The degradation of solutions of ethylene dibromide, bromoethanol, and ethylene oxide under direct irradiation using a 240 W Hanovia medium-pressure mercury lamp was observed with time. The reactor, as described above, was charged with 600 mL of an aqueous solution in air. The entire apparatus was placed in a water bath held at 22 degrees C. Aliquots of the reaction solution were taken with time. The concentration of Br^- was determined potentiometrically from 3 mL aliquots of the reactions in the manner previously described (2). Ethylene Dibromide, (138 degrees C, 8.0 min), bromoethanol (138 degrees C, 4.0 min), and ethylene oxide (90 degrees C, 3.0 min) were determined from 1-µL reaction aliquots by direct flame ionization gas chromatography on a 3.5ft $^1/_8$ inch Poropak P column containing 3% DEBS and 6% DC-710. Ethylene oxide was monitored on a 2ft $^1/_8$ inch Poropak R column (90 degrees C,3 min).

Quantitation was accomplished by comparison with authentic standards over a linear range of machine response.

The nature of the photoproducts was confirmed by GC-MS. A 4ft Poropak R column was directly connected to a quadrupole mass spectrometer. MS results: Bromoethanol (parents 126, 124) 126, 124; (CH_2CH_2-OH, 45) 45; ethylene oxide (parent 44) 44.

Relative rates of EDB and ferrioxalate were also assessed under sunlight irradiation. For this purpose stock solutions of EDB and ferrioxalate were placed in sealed quartz tubes. The latter were placed on the roof and sampled for Br^- and Fe^{II}.

RESULTS: Results establish a quantitative reaction sequence for the photolytic process. The first step is hydrolysis with a calculated rate constant of $1.5 \times 10^{-3}\ s^{-1}$ ($t_{1/2} = 7.6$ min). This is followed by a slower hydroxylation step with a calculated rate constant of $1.8 \times 10^{-4}\ s^{-1}$ ($t_{1/2} = 64$ min). The steps are shown by the following equations:

$$BrCH_2CH_2Br \xrightarrow[H_2O]{h\nu} BrCH_2CH_2OH + H^+ + Br^-$$

$$BrCH_2CH_2OH \xrightarrow[H_2O]{h\nu} \overline{CH_2CH_2O} + H^+ + Br^-$$

Ethylene oxide is well known to hydrolyze in aqueous solution to ethylene glycol (See equation below). The process is general acid or base catalyzed (3). The rate of hydrolysis is not enhanced by light. At pH 7, $t_{1/2}$ is approximately 10 days.

$$\overline{CH_2CH_2O} \xrightarrow[H_2O]{H^+,\ OH^-} HOCH_2CH_2OH$$

The relative rates of the light enhanced hydrolysis and hydroxylation steps compared to the rate of reduction of potassium ferrioxalate ($k_{RX}/k\ Fe^{III}O_x$) are 32 for EDB and 3.8 for bromoethanol, respectively. With sunlight irradiation EDB reacts 2.7 times faster than ferrioxalate. An estimate of the rate for Br^- release from EDB based on 53 days (and nights) of exposure to roof sunlight, (10% conversion) corresponds to a $t_{1/2}$ of approximately 380 days. No direct photolysis of any consequence can be expected under environmental conditions.

STATISTICAL METHODS: For Ethylene Dibromide and bromoethanol, the rate of reaction was assessed from linear first-order plots of the disappearance of EDB with time. Reproducibility was ± 10% and ±5% for EDB and Bromoethanol, respectively.

DATA QUALITY: Although the report lacks much of the information that is required by established protocols and guidelines, the study is scientifically sound and valid. The results delineate the processes involved in the photolysis of EDB and the relative rates of these processes.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The study is reasonably well documented and meets the generally accepted scientific principles for carrying out a photolysis study. The study is useful for determining the breakdown processes, relative rates of breakdown processes and products.

REFERENCES:

1. Parker, C. A., Proc. R. Soc. London A 1953, A220, 104.

2. Castro, C. E., Belser N. O., J. Agri. Food Chem., 1983, 29, 1005.

3. Long, F. A.; Pritchard, J. G., J. Am Chem. Soc., 1956, 78, 2663.

2. REPORT NUMBER: BD-1

STUDY TYPE: Aerobic metabolism study in soil

STUDY TITLE: United States Patent: Biodegradation of Halogenated Aliphatic Hydrocarbons

AUTHORS: John T. Wilson, Jr. et al.

REPORT DATE: Published as a patent, December 18, 1987.

TESTING FACILITY: Not given.

STUDY NUMBER: Not given. This study was composed of three (3) examples given in the patent (Patent Number 4,713,343).

SPONSOR: Wilson, Jr. et al

STUDY OBJECTIVES: The studies reported in the patent issuance document were used as supporting evidence for the effectiveness of the patented method for removal of residues of low molecular halogenated aliphatic hydrocarbons from ground and surface water under aerobic conditions.

RECOGNIZED METHOD: The authors indicated that this was a unique process for remediation of contaminated ground or surface water. The reference OECD guideline is OECD 307.

GLP: Pre-GLP.

TEST MATERIAL: Numerous low molecular weights halogenated aliphatic hydrocarbons which included ethylene dibromide (EDB).

Purity: Purity and the source suppliers of the starting materials were not given in the report

CONTROLS: As a comparison of the biological effectiveness of the microorganisms in degrading the halogenated aliphatic hydrocarbons, the test column was sterilized using 2 grams of sodium azide in water with a concentration of the halogenated aliphatic hydrocarbon being treated.

CONCENTRATIONS OF TEST SUBSTANCES: The report did not give the specific concentrations of the starting halogenated aliphatic hydrocarbons

EXPOSURE PERIOD: This was a continuous process. The results (i.e. rate of removal) were given per hour.

EQUIPMENT: No specifications of the types equipment used in the study were given.

TEST PROCEDURE: In the method, the use of natural occurring microbes (having the ability to use a class of enzymes called monooxygenases) to degrade low molecular halogenated aliphatic hydrocarbons. Sandy soil was packed into a glass column to a depth of 150 cm. A stream of air containing 0.6 percent natural gas by volume was passed over the head of the column. Three weeks were allowed for acclimation, after which the soil received water, which contained the specific halogenated aliphatic hydrocarbon. The concentrations of the halogenated aliphatic hydrocarbon in the column effluent were monitored for two weeks. The water containing the halogenated aliphatic hydrocarbon was applied at the rate of 21 cm per day. The elution volume of the column was 41 cm of water. Water entering and leaving the column pass through 16 mL screw cap test tubes that were sealed with a Telfon faced septum. As appropriate, the tubes were removed for analysis of the halogenated aliphatic hydrocarbon according to the USEPA test method no. 601 (1). The tubes were then left in place long enough for 15 to 25 flushings before the samples were taken. With the exception of the sampling method, the construction and operation of the column was the same as described by Wilson et al (2).

The first study used trichloroethylene to demonstrate the effectiveness of the method.

To confirm that the increased removal represented biological activity, the column was poisoned with water that contained 224 μgrams of trichloroethylene and 2 gram per liter of sodium azide. The amount of trichloroethylene passing through the column in the effluent was measured.

A second study was carried out using radiolabelled [^{14}C]trichloroethylene to identify the biotransformation products formed. After a second column was acclimated to natural gas, it was then dosed with a solution of [^{14}C]trichloroethylene. After 1.6 solution volumes of water had been applied, 15.8 ± 0.3 percent (alpha= 0.05) of the applied radiolabel appeared in the column effluent. This label could not be purged from the solution by vigorous aeration when the pH was adjusted to 11. At least 97 percent (alpha = 0.05) of the label precipitated with barium hydroxide indicating the biotransformation product was mainly ^{14}CO2.

The third study demonstrates the effectiveness of the method on twelve halogenated aliphatic hydrocarbons.

STATISTICAL METHODS: There is an implied statistical analysis of the results. However, the patent did not indicate how the data was handled. The percent removed was calculated as the material that passed through a living soil column divided by the material that passed through soil killed with 0.1% sodium azide times 100.

RESULTS:

In the first study, the removal of trichloroethylene was extensive, with less than 5 percent of the applied trichloroethylene passing through the soil column. After the sodium azide treatment, the amount of trichloroethylene passing through the soil increased significantly.

The second study showed the biotransformation products were mainly CO_2.

The results of the third study are given below:

Compound	% Removed[a]	Rate of Removal[b] Hr^{-1}	Rate of Removal at 95% Confidence hr^{-1}
Trichloroethylene (TCE)	95	0.95	0.75
Trans-1,2-dichlorehtylene	>94	>0.86[c]	-
Cis-1,2-dicloroethylenedichloroethylene	>98	>1.2[c]	-
1,2-dibromoethane (EDB)	94	0.86	0.42
Dichloromethane	94	0.91	0.41
Chloroform	83	0.55	0.29
1,2-Dichloroethane	85	0.60	0.56
1,1-Dichloroethane	76	0.44	0.41
1,1,2-Trichloroethane	55	0.25	0.22
1,1,1-Trichloroethane (TCA)	19	0.067	0.023
Carbon Tetrachloride	44	0.18	0.13
Tetrachloroethylene (PCE)	31	0.11	0.085

[a] Material that passed through a living soil + material that passed through soil killed with 0.1% sodium azide x 100.
[b] Assumes all the biological activity is uniformly distributed in the top 10 cm of soil.
[c] Concentrations were below detection units after passage through living soil.

DATA QUALITY: There is not way to confirm the data quality. The report is a summary of the nature of the method and the results.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [x]
4. not assignable [ ]

REASON: The study is not useful to determine the rate of aerobic biodegradation. The conditions of the study and the data are not well documented. The study does demonstrate that should aerobic biodegradation take place in the environment, the biotransformation product is likely to be mainly CO_2.

REFERENCES:

1. United States Environmental Protection Agency test method No. 601, (U.S. Environmental Protection Agency, 1982, Methods for Organic Chemical Analysis of Municipal and Industrial Waste Water, EPA 600/4-82-057, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268).
2. Wilson et al., J. Environ. Qual., Volume 10, pages 501-506, 1981.

3. **REPORT NUMBER: HY-1**

STUDY TYPE: Rate of Hydrolysis

STUDY TITLE: Rates of Hydrolysis of Ethylene Dibromide (EDB)

AUTHORS: Not given.

DATE OF REPORT: August 1984

TESTING FACILITY: Applied Biology, Inc., Decatur, Georgia

STUDY NUMBER: Report Number: AB-544

SPONSOR: Industrial Committee of the Ethylene Dibromide Research

STUDY OBJECTIVE: This study was designed to determine hydrolysis rates of ethylene dibromide (EDB) at two temperatures, each with three pH regiments. These six test regimes, all conducted in darkness, were expected to provide estimates of EDB half-life and the applicable rate law.

RECOGNIZED METHOD: Comparable to OECD guideline 111.

GLP: Pre-GLP.

TEST MATERIAL: Ethylene dibromide (EDB). Solutions of EDB in aqueous buffers were prepared as follows. The EDB was weighed in a small glass thimble and was dropped in a 1 Liter volumetric flask filled to the mark with the corresponding buffer. A magnetic stirrer bar was added; the flask was then stoppered and agitated overnight or until the glass thimble was broken into small pieces and the EDB completely dissolved. The water and glassware were sterilized in an autoclave. Purity and the source supplier of the EDB was not given in the report

CONTROLS: Several ampules of standard EDB solution (96 ppm) in distilled water were sealed and stored in a refrigerator at 4°C.

CONCENTRATIONS OF TEST SUBSTANCES: Three solutions were prepared one in the buffer of pH 5 (EDB concentration of 95.6 ppm); the second in the buffer of pH 7 (EDB concentration of 88.8 ppm); and the third in the buffer of pH 9 (EDB concentration of 85.1 ppm). The report does give the composition of the buffers or whether the buffers were sterilized prior to using them in the study.

The EDB concentration in the buffer solutions was calculated by comparing the area of the sample peak to the area of the reference standard of known concentration.

STATISTICAL METHODS: The half-life for the decomposition of EDB was calculated assuming the reaction rate was between zero order kinetics and first order kinetics, owing to the nature of the molecule.

Zero Order: A plot of concentration vs. time was made and the half-life ($t_{1/2}$) determined from this plot.

First Order: Assuming the hydrolysis of EDB follows first order reaction, the half-life was calculated from the formula

$$T_{1/2} = \frac{0.693}{K}$$

EXPOSURE PERIOD: Samples were taken on day 0, 30, 60, 95, and 140 days.

EQUIPMENT: The analysis for volatile organic byproducts was done using a purge-and-trap module (Tekmar) interfaced with a Finnigan GC/MS (OWA-1000).

TEST PROCEDURE: Ampules of each buffer solution were placed in incubators maintained at 25 ± 1°C or 45 ± 1°C. One ampule for each pH and temperature (total of six) was withdrawn from the incubators and analyzed for EDB concentration on day 0, 30, 60, 95, and 140 days. Each ampule was broken and 0.4 µL samples were withdrawn with a microsyringe for chromatographic analysis. Six replicate analyses were performed from each ampule and the mean of all six analyses was calculated and used as the concentration at the day.

The analysis for volatile organic byproducts identified only ethylene bromide (CH_2-CHBr). Its concentration could not be assayed due to losses of evaporation upon breaking the sample ampule and to unknown trapping efficiency of the Tenax trap for ethylene bromide.

RESULTS:

- The rate of hydrolysis of EDB is very slow at 25 degrees C, but increases as the pH decreased from 9 to 5.
- The rate of hydrolysis at 45 degrees C is several times faster than at 25 degrees C at all three pH's, and the kinetic order approaches one. At 45 degrees C the rate increased with increasing pH.
- The primary reaction of EDB decomposition appears to be dehydrohalogenation, at least at 45°C and pH 9.
- The product of debromination, ethylene (CH_2-CH_2), was not detected.
- The percentage of EDB hydrolyzed after 140 days was 0-13% (@ 25 degrees) and 33-42% (@ 45 degrees).

DATA QUALITY: Study follows recognized scientific protocols for hydrolysis studies. The composition of the buffers and whether they were sterilized was not provided. Also, daily recording of the temperatures and samples of the GC/MS, which were conducted, were not given. These deficiencies, although important, do not detract from the results obtained from the study.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The study follows accepted scientific principles, acceptable for assessment. The report did not give the composition of the buffers; whether the buffers were sterile; temperature was not recorded daily and samples of the chromatography analyses were not provided.

REFERENCES: None

4. **REPORT NUMBER: BD-2**

STUDY TYPE: Hydrolysis and anaerobic degradation in soil, sludge and groundwater.

STUDY TITLE Chemical and Microbial Degradation of 1,2-Dibromethane (EDB) in Florida Ground Water, Soil, and Sludge.

AUTHORS: R. A. Wentraub, G. W. Jex, and H. A. Moye

DATE OF REPORT: 1986

PUBLISHED: ACS Symposium Series, 315. 1986. Kap 15, pp 294-310.

TESTING FACILITY: Pesticide Research Laboratory, University of Florida, Gainesville, FL 32611

STUDY NUMBER: Not given; published data.

SPONSOR: Florida Department of Environmental Regulation (contract EDB 005)

STUDY OBJECTIVES: This study evaluates the degradation of EDB by hydrolysis in groundwater samples and by microbial activity in soil samples collected from north central and northwestern regions of Florida. Laboratory experiments were performed with natural samples in order to make qualified estimates of the persistence of EDB in the subsurface environment and to identify the products of degradation. The potential for biotransformation of the chemical by two different sludge preparations was also investigated.

RECOGNIZED METHOD: A specific guideline was not referenced. The experiment followed the scientific principles and procedures used in EPA/OPP and OECD accepted guidelines, such as OECD 307..

GLP: Not stated.

TEST SUBSTANCE: EDB was analytical grade with a purity of +99% supplied by Aldrich Chemical, Milwaukee, Wisconsin. ^{14}C-EDB (approximately 500 µCi/g) was obtained from Amersham, Arlington Heights, Illinois. The purity of the chemical or radiochemical purity was not given.

OTHER MATERIALS: Information on the source, purity and characteristics of all chemicals used in making the buffers were provided. Analytical grade chemicals were used.

CONTROLS:

Ground water Degradation Kinetics Study:

At least 2 samples in each incubation trial were fortified with ^{14}C-EDB (approximately 500 µCi/g).

For the gas chromatography, standard curves of detector response over the range of 20 to 1500 pg/µL of EDB were constructed and used for quantitation using linear regression least squares analysis and were prepared daily.

For bromide analysis by absorbance, standard aqueous solutions of bromide were assayed to construct a standard curve over a range of 50 to at least 1000 ppb.

For scintillation counting, quenching was evaluated by comparing additions of the fortified waters or hexane extracts to additions of known amounts of ^{14}C-toluene. Efficiencies and precision of extraction of EDB from the waters were evaluated in a similar fashion.

Soil and Sludge Degradation Experiments:

An unfortified soil and three sterilized fortified soil replicates were analyzed at each sampling.

CONCENTRATION OF TEST SUBSTANCES: Groundwater samples and laboratory deionized water were fortified with EDB to concentrations of 10 to 100 ppb.

For the soil sludge experiments, fortification was carried out with EDB to a concentration of 400 ppb using an alcohol solution of ^{14}C-EDB to give 4000-5000 dpm/mL as a tracer.

EXPOSURE PERIOD: Not specified for the groundwater degradation kinetics study. In the soil and sludge experiments, the soils and sludges were analyzed at 1, 5, 10, and 30 days then monthly thereafter for seven months.

TEMPERATURE: The hydrolysis portion of study was carried out at 40, 50, 60, 70, and 80 ± 0.5 degrees C in the soil and in the sludge experiment the temperature was 25 degrees C.

TEST PROCEDURE:

Groundwater Degradation Kinetics Study:

Groundwater obtained from shallow wells in three north central and northwest Florida counties (Polk, Highlands, and Jackson) and laboratory-deionized water was fortified with EDB to concentration of 10 or 100 ppb. Samples were sterilized, microbial activity eliminated, and incubated at 40, 50, 60, 70, and 80 ± 5 degrees C. Aliquots were transferred to test tubes, hexane added, mixed for 5 minutes and sampled for gas chromatographic (GC) analysis.

At least 2 samples in each incubation trial were fortified with ^{14}C-EDB and periodically sampled for total ^{14}C activity to check the integrity of the system.

A series of 5 x 10^{-3} buffer systems were used to maintain the EDB fortified waters at pH values ranging from 4.0 to 9.0. The buffers included borax/succinic acid, phthalate/NaOH, borate/NaOH, borax/phosphoric acid, and carbonate/bicarbonate. Incubations were conducted at 62 degrees C.

Ethylene glycol concentrations in water were determined by GC analysis. The quantity of formaldehyde in the aqueous solution was also determined.

A Standard Methods Procedure (no. 405 C) was followed to measure the bromide ion in aqueous solution. The bromide ion was oxidized by chloroamine T to bromine that brominates phenol red, and the absorbance of the reaction mixture was read at 590 nm.

Soil and Sludge Degradation Experiments:

Soils were sampled from three sites in Florida where water from wells had been contaminated with EDB. The EDB degrading ability of the indigenous microflora were examined. Samples from each site were collected at depths of 1 and 3 meters.

Two sludge sites were used to study the EDB degrading potential of a broad spectrum of microflora. One sludge sample contained a rich flora of facultative organisms. The second sludge sample was known to contain methanogenic flora.

The bottle-filling and incubation procedures were adapted from Bouwer and McCarty (2) and the medium was that of Alexander and Lurtigman (3). The sterilized medium (121°C. 15 psi, 20 min) was boiled and then flushed with N_2 while cooling and fortified with EDB to a concentration of 400 ppb. At each sampling, an unfortified soil along with three fortified and three sterilized fortified soil replicates were analyzed. At each sampling period, three 20 ml portions from each bottle were removed for CO_2 analysis.

RESULTS:

Groundwater Degradation Kinetics Study:

All kinetic plots constructed from the data indicated that in the water tested, the disappearance of EDB from solution at all temperatures (40 to 70 degrees C) followed simple pseudo-first order kinetics. The rate constants observed in the different waters varied only slightly and indicate that neither acid nor base-catalyzed hydrolysis is favored within the pH range examined (pH 4-9). At pH 5 and 8, an increase in the rate constants of about 10% was observed, but because these portions of the plot were not consistent with a pH-dependent trend, i.e., a constant slope over a considerable pH range, these deviations can be attributed to specific contributions of the buffer type used.

STATISTICAL METHODS: Degradation rate constants were obtained by linear regression least squares analysis of plots of log % EDB remaining versus time. Pseudo-first order rate constants were used to generate Arrhenius plots (log rate constant versus 1/T degrees K) to estimate activation energies (E_a) and to make extrapolated estimates of rate constants and half-life values at ambient temperature.

The differences in the rates of degradation were evident in several groundwater samples. In contrast, the observed degradation rates in deionized water were identical. These results suggest that the constituents of groundwater may have an influence on the hydrolysis of EDB.

At elevated temperature (60, 72, and 80 degrees C) the decrease in ^{14}C-activity partitioned in the hexane phase after extraction paralleled the EDB decline determined by GC. Extractions of the aqueous phase did not result in detection of other brominated compounds. Nor were purgeable brominated compounds detected in the aqueous phase by GC/MS. The major hydrolysis products measured were EDB, ethylene glycol, and the bromide ion. During these incubations, these products accounted for 60 to 100% of the initial EDB.

Hydrolysis of EDB is a two-step process: first, the removal of bromide in the presence of water to form bromoethanol and second, the removal of the second bromide ion to form ethylene glycol. The conversion of EDB to ethylene glycol and bromide ion was essentially complete after 7 days.

Prompted by a study that showed the EDB could be oxidized under anhydrous conditions to formaldehyde by the action of superoxide ion (6), water solutions were fortified with EDB and incubated at elevated temperatures for a period of time. Analysis found low consistent levels of formaldehyde, but only after all the EDB had been hydrolyzed. Studies conducted with natural and deionized water fortified to 10 ppm with ethylene glycol and

incubated at 85 degrees C showed that the amounts of formaldehyde detected varied from about 350 ppb to 2 ppm after 40 days of incubation. These findings taken together indicate that hydrolysis of EDB is required as a first step for formaldehyde production and that EDB is not converted to formaldehyde by direct oxidation as was found in the superoxide study

Soil and Sludge Degradation Experiments:

Soils and sludges did not show evidence of CO_2 production from EDB incubations. This result is consistent with negative results reported by Bouwer and McCarty (7,8) for CO_2 production.

In the methanogenic sludge, there was a decrease in dpm/mL found in the hexane extract with time, indicating the EDB was being degraded. The amount of dpm/mL in residual water, for both natural and sterile sludges indicates little dissolved CO_2 or other water-soluble degradation product(s) is being formed. This suggests the formation of a volatile product or products during incubation.

The results from the facultative sludge samples were similar to the methanogenic sludge. In 60 days, all the EDB was degraded and little radioactive material remained in the residual water after the triple hexane extraction. Similarly, the sludge produced the same gaseous products, of which only the ethylene was radioactive.

These results confirm the hypothesis of Bouwer and McCarty (7) that the water-insoluble volatile product derived from their EDB seeded culture incubations is ethylene. The results from these studies indicate a gradual decline of EDB prior to 40 days with a rapid decline thereafter.

The Florida soils tested were only weakly capable of degrading EDB under anaerobic conditions (e.g. 40% in labeled and non-labeled EDB after 7 months). No CO_2 was produced and there was no more ^{14}C-activity in the residual water after hexane extractions than for the sterile preparations. This indicates that the degradation product or products are volatile, such as ethylene. All other soils failed to degrade EDB under similar conditions over equally long incubation periods. This implies that either appropriate organism(s) are not present or the soils contained insufficient secondary carbon sources necessary to maintain co-metabolism.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: This study is well documented, meets generally accepted scientific principles, and is acceptable for assessment. It generally follows the procedures of a guideline study. Although detailed documentation of some parameters were omitted, they do not detract from the scientific merits of the results reported.

REFERENCES:

1. "Standard Methods for the Examination for Water and Wastewater", 15th ed., APHA-AWWA-WPCF, p.261, (1980).
2. Bouwer, E. J.; McCarty, P. L., Transformations of halogenated organic compounds under denitrification conditions. J. Appl. And Environ. Micro., 45(4)1286, (1983).
3. Alexander, M.; Lurtigman, B. K., Effect of chemical structure on microbial degradation of substituted benzenes, J. Agric. And Fd. Chem., 14,410 (1966).
4. Perdue, E. M.; Wolfe, N. L., Prediction of buffer catalysis in field and laboratory studies of pollutant hydrolysis reactions, Environ. Sci. and Tech., 17 (11) 635 (1983).
5. Lyman, W.J., solubility in Water in "Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds;" Lyman, W.J.; Reehl, W.F.; et al, eds., McGraw-Hill; New York (1982).
6. Schwarzenbach, R.P.; Giger, W.; et al, Groundwater contamination by volatile halogenated alkanes: abiotic formation of volatile sulfur compounds under anaerobic conditions. Environ. Sci. and Tech., 19, 322 (1985)
7. Bouwer, E. J.; McCarty, P. L., Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions, Appl. And Environ Micro., 15(4)1286 (1983)

8. Bouwer, E. J.; McCarty, P. L., Ethylene Dibromide under methanogenic conditions, Appl. And Environ Micro., in press (1985).
9. Calderwood, T. S., Sawyer, D. T., Oxygenation by superoxide ion of 1,2-dibromo-1,2-diphenylethane, 2,3-dibromobutane, ethylene Dibromide (EDB), and 1.2-dibromo-3-chloropropane (EDBCP), J. Am. Chem. Soc., 106,7185 (1985).

5. REPORT NUMBER: MOD-1

STUDY TYPE: Analytical Method Development for Residual EDB

STUDY TITLE: Determination of 1,2-Dibromoethane (EDB) in Field Soils: Implications for Volatile Organic Compounds.

AUTHORS: B. L. Sawhney, J. J. Pignatello, and S. M. Steinberg

DATE OF REPORT: Published in J. Environ. Qual., vol. 17, no. 1, 1988

TESTING FACILITY: Not given

STUDY NUMBER: Not given

SPONSOR: Not given

STUDY OBJECTIVES: To critically examine several likely methods for determining residual EDB in the soil leading to the development of a satisfactory method.

RECOGNIZED METHOD: The method developed is applicable to aerobic and anaerobic transformation in soil (OECD 307), but is an analytical method as opposed to an analysis of degradation.

GLP: Pre-GLP

TEST SUBSTANCE: ^{14}C-EDB (204 x 10^7 Bq/mmol) Obtained from Amersham

OTHER MATERIALS: Not given

Soil Characteristics:

Soil Names	Cheshire fine sandy loam	Agawam fine sandy loam	Enfield silt loam
Description	Coarse-loamy, mixed, mesic Typic Dystrochrepts	Coarse-loamy over sandy or sandy-skeletal, mixed, mesic Typic Dystrochrepts	Coarse-silty over sandy or sandy-skeletal, mixed, mesic Typic Dystrochrepts)
Source	Lock Farm of the Connecticut Agr. Exp. Sta.	Tobacco farm in Warehouse Point, Ct	Tobacco farm in Broad Brook, Ct
EDB use	Fumigated in 1985 at 67 kg/ha	According to agricultural practices. Last used I 1983	According to agricultural practices. Last used I 1973
Percent			
Sand	60	46	50
Silt	34	44	45
Clay	6	10	5
Organic Carbon (g/kg)	11.1	16.1	16.5

CONTROLS: The EDB was identified in extracts of the field soils by GC/MS by comparison with analytical compound.

CONCENTRATION OF TEST SUBSTANCES: Not Applicable

EXPOSURE PERIOD: Not Applicable

EQUIPMENT: Hewlett Packard 5988A GC/MS. The mass spectrometer was operated in the electron impact mode (70eV). These signals represent the loss of Br from the parent ion. The limit of detection was 10 pg EDB.

Hewlett Packard 7675A purge and trap unit with N_2 gas for different periods of time either at 40 or 80°C. The EDB was analyzed with a Hewlett Packard 5840 gas chromatograph using a stainless steel column and flame ionization detector.

For thermal desorption, hexane was analyzed for EDB by GC isothermally at 80°C using a 2 m by 4 mm o.d. column of 155 OV17 on Chromosorb WHP (80/100 mesh) and a ^{63}Ni electron capture detector with a 40 mL/min flow of 5% methane in argon. The detection limit was 1.5 pg EDB (0.3 µg/L EDB in hexane).

TEST PROCEDURE: For purge and trap, a 1 gram soil sample was analyzed for EDB by gas chromatography using a flame ionization detector.

Thermal desorption removal of EDB at 100 to 200°C was carried out by passing a stream of N_2 at 20 mL/min through a soil column. The detection limit was 1.5 pg EDB.

In the solvent extraction study, the soil was extracted with methanol, acetone, acetonitrile, hexane, or hexane-water mixtures at different temperatures.

Sonication-extraction was carried out on 30 g soil in 100 mL methanol in a 400-mL beaker.

RESULTS: The authors compared several methods for determination of EDB in the field samples: purge and trap, thermal desorption, and various solvent extraction methods. The only satisfactory one was a solvent extraction technique.

The purge and trap method, as prescribed by EPA Method 8240 for estimating VOCs in soils, removed only small amounts of EDB. Purging at higher temperature and longer periods of time increased the release of EDB. Nonetheless the amount released was <11% of the total found by the recommended solvent extraction method.

In the thermal desorption method, essentially no EDB was desorbed from the field-contaminated soil over the temperature range studied.

These results demonstrated that thermal desorption methods are not suitable for determining residual EDB in soils.

A comparison of the ability of different organic solvents to extract EDB showed that two 24 hours extraction with methanol at 75°C recovered essentially 100% of the residual EDB.

The use of Sonication-extraction method (3) with methanol for 1.5 minutes total Sonication time recovered only 12%, based on total EDB removed by the recommended method below.

The study results indicate the following procedure is the best method for removal of EDB residual from soil. Weigh 5 g of soil in a 40-mL glass screw-cap vial, add 25 mL methanol, and cap firmly. Invert the vial and mark the level of liquid as a reference for determining any leak during heating. Place the vial inverted in an incubator at 75°C for 24 hour. After 24 hours, allow the vial to cool. After cooling, check the level of liquid and discard any vial where loss in volume is indicated. Centrifuge (1500 rpm for 10 min) and transfer the supernatant into a 200-mL flask. Resuspend the soil in 25 mL methanol, centrifuge, and transfer the supernatant to the flask. Add 30 mL hexane and 100 mL distilled water to the combined methanol extracts. Shake vigorously for 30 seconds and allow the phases to separate. The volume of the upper hexane layer is not appreciably different from the volume of hexane added. Analyze the hexane layer by GC and multiply the calculated total EDB by 1.13 to account for EDB left in the water-methanol layer. The detection limit is 1.8 µg/kg using a ration of 5 g soil to 25 mL methanol.

STATISTICAL METHODS: None

DATA QUALITY: The method developed examines several published analytical methods in order to present the best method for analyzing soil samples for EDB residues. The results appear to support the recommendation for method analysis. It does not satisfy a SIDs endpoint but is, nonetheless an acceptable scientific procedure.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The authors evaluated several methods for removing EDB residues from soil in order to determine the best analytical method. The study was sufficiently documented for a method development.

REFERENCES:

1. Steinberg, S. M., J. J. Pignatello, and Sawhney, B. L., 1987. Persistence of 1,2-dibromoet;hane in soils: Entrapment in intraparticle micropores, Environ. Sci. technol.
2. Federal Register, 1979, Fed. Regist. 44(233):69532-69539.
3. U.S. Environmental Protection Agency, 1982, Test methods for analysis of solid waste: Physical/chemical methods. SW-846 2nd ed., Office of Solid Waste and Emergency Response, Washington, DC.

6. REPORT NUMBER: BD-3

STUDY TYPE: Information Review

STUDY TITLE: Environmental Chemistry of Ethylene Dibromide in Soil and Ground Water

AUTHORS: J. J. Pignatello and S. Z. Cohen

DATE OF REPORT: Not given.

PUBLISHED: Reviews of Environmental Contamination and Toxicology, Vol. 112, 1990 Springer-Verlag, New York, Inc.

TESTING FACILITY: Not Applicable

DATES OF EXPERIMENTAL WORK: Not Applicable

STUDY NUMBER: Not Applicable

SPONSOR: Not Applicable

STUDY OBJECTIVES: Not Applicable

RECOGNIZED METHOD: The paper addresses the following endpoints: OECD 103, Melting Point; OECD 104, Vapor Pressure; OECD 107/117, Octanol/Water partition coefficient; OECD 105, Water Solubility; and OECD 106, Adsorption/desorption to soil.

GLP: Not stated.

TEST SUBSTANCE: Ethylene dibromide

OTHER MATERIALS: Not Applicable

CONTROLS: Not Applicable

CONCENTRATION OF TEST SUBSTANCES: Not Applicable

EQUIPMENT: Not Applicable

TEST PROCEDURE: Not Applicable

RESULTS: This paper is a review of existing information taken from other scientific papers. There is no way to know the validity and soundness of the information in this paper.

The following are a listing of properties of EDB that are relevant to its environmental fate and transport.

Boiling point	131.7°C	Timmermans and Martin (1926)
Specific gravity	2.178 g/cm^3	Timmermans and Martin (1926)
Vapor pressure	10.8 mmHg @ 25 degrees C	Call (1957a)
	7.7 mmHg @ 20 degrees C	Call (1957a)
Water Solubility	4250 mg/L @ 25 degrees C	Stephen and Stephen (1963)
	3370 mg/L @ 20 degrees C	Call (1957 b)
Henry's Law Constant	0.0246 mg/L @ 20 degrees C	Call (1957 f)
Octanol/Water Partition Coefficient	1.93	Steinberg et al. (1987)

The authors summarize hydrolysis studies by several authors and note that at normal environmental temperatures, the half-life of EDB is at least 2 years, with ethylene glycol the major product. They also noted that EDB may react with naturally occurring sulfur nucleophiles (e.g. hydrogen sulfide and bisulfide ion) in ground water (anaerobic). The impact of microbial metabolism was also explored. A number of pure and mixed cultures from soil, sediment and aquifer microcosms can degrade EDB. This occurs in both oxic and anoxic conditions. It is dehalogenated to ethylene gas under methaneogenic conditions. Concentration in the environment is a factor since EDB is toxic to bacteria, suggesting this activity is relevant when EDB is greater than a few tenths of a ppm. Such conditions are likely to exist after soil fumigation. Monitoring results from several States performed in the 1980's were also presented and summarized. However, comparisons of these results is difficult because of the variation is study design and statistical basis. Nonetheless the authors conclude that EDB is present in groundwater samples resulting principally from its use as a soil pesticide, and secondarily from spills or leaks of leaded gasoline when used as an additive.

STATISTICAL METHODS: Not Applicable

DATA QUALITY: This is a summary report of various aspects of the soil transformation properties of EDB which were examined experimentally and published by other authors. Their work and results are summarized and referenced in this report.

RELIABILITY: Not Applicable

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The paper is a review of available information on EDB. It relies on other scientific documents as the source of the information.

REFERENCES:

1. Call F., (1957a) Determination of the vapor pressure of ethylene dibromide. J. Sci. Food Agric. 8:81-85.
2. Call F., (1957b) The diffusion of ethylene dibromide. J. Sci. Food Agric. 8:86-89.
3. Call F., (1957f) The mechanism of sorption of ethylene dibromide on moist soils, J. Sci. Food Agric. 8:630-639.
4. Steinberg, S. M., Pignatello, J. J., Sawhney, B. L., (1987) Persistence of 1,2-dibromoethane in soils: entrapment in intraparticle micropores. Environ. Sci. Techn., 21: 1201-1208.

5. Stephen, H., Stephen, T., (1963), Solubilities of inorganic and organic compounds. Macmillan, New York, NY.
6. Timmermans, J., Martin, F., (1926) The work of the International Bureau of Physical-Chemical Standards. II. Study of twenty hydrocarbons and halogen derivatives, J. Chem. Phys., 23:747-787.

7. REPORT NUMBER: BD-4

STUDY TYPE: Anoxic transformation study

STUDY TITLE: Transformations of Halogenated Organic Compounds Under Denitrification Conditions

AUTHORS: E. J. Bouwer and P. L. McCarty

DATE OF REPORT: Published in Applied and Environmental Microbiology, April 1983, vol. 45, No.4, pp 1295-1299.

TESTING FACILITY: Environmental Engineering and Science, Department of Civil Engineering, Stanford University, Stanford, California, 94305

STUDY NUMBER: Not given.

SPONSOR: This work was supported in part by grant no. EPA-R-808034010, Office of Research and Development, U. S. Environmental Protection Agency and by a National Science Foundation Graduate Fellowship.

STUDY OBJECTIVES: To study the transformation of several organic solvents at concentrations commonly found in surface and groundwater under anoxic conditions in the presence of denitrifying bacteria.

RECOGNIZED METHOD: Does not conform to any recognized method, but it is most comparable to OECD 302, Inherent biodegradability.

GLP: Pre-GLP

TEST SUBSTANCES: Reagent grade compounds were used: Naphthalene (NAPH) and 1,4-dichlorobenzene (1,4-DCB); 99+% 1.2- and 1,3-DCB, 1,2,4-trichlorobenzene (1,2,4-TCB) and ethylbenzene (EB); Chlorobenzene (CB), bromodichloromethane (BDCM) and 96% bromoform (BF); chloroform (CF) and carbon tetrachloride (CT); 1,1,1-trichloroethane (1,1,1-TCE) and 1,2-dibromoethane (1,2-DBE); Dibromochloromethane (DBCM).
The following radiochemicals were used: 1,4-dichloro[U-^{14}C]benzene (16.1 mCi/mmol), [^{14}C]CT (22 mCi/mmol), and 1,2-bromo[U-^{14}C]ethane (14.6 mCi/mmol).

OTHER MATERIALS:

The general growth medium used contained the following (per Liter): 100mg of ethanol, 450 mg of $NaNO_3$, 100 mg of K_2HPO_4, 20 mg of $MgSO_4 \cdot 7H_20$, 5 mg of $FeSO_4 \cdot 7H_20$, 2 mg of $CaCl_2$, 0.2 mg of $MnCl_2 \cdot 4H_20$, and 0.1 mg of $NaMoO_4 \cdot 2H_20$. An excess of nitrate was provided to maintain redox conditions between those for aerobic and methanogenic decomposition

CONTROLS: Sterile controls were used

CONCENTRATION OF TEST SUBSTANCES:

Batch 1 was composed of EB, NAPH, CB, 1,2-DCB, 1,3-DCB, 1,4-DCB, AND 1,2,4-TCB at an initial concentration between 40 and 114 µg/liter.

Batch 2 was composed of CF, CT, 1,1,1-TCE, BDCM, DBCM, BF, AND 1,2-DBE at nominal initial concentrations of 60 µg/liter. Carbon-14-labelled 1,2-DBE was also included (~3,000 dpm/mL)

The test substances were dissolved in ethanol at a concentration of 40 mg/mL of ethanol. The aqueous solution added to the bottles was prepared by diluting a stock solution of the aromatic compounds in ethanol with deionized water.

EXPOSURE PERIOD: 11 weeks at 25degrees C

TEST PROCEDURE: For Batch 1, sterile 160-mL serum bottles were purged with N_2 and completely filled with deoxygenated medium with an anaerobic pipette (1). Except for sterile controls, the medium was seeded with 2 mL of primary sewage effluent per liter. A sample of the dilute aqueous solution containing a mixture of the aromatic compounds (batch 1) and 1,4-dichloro[U-^{14}C]benzene tracer (~2 µCi/mL) was added directly to each bottle, and sealed. All bottles were incubated without agitation in the dark at 25°C and were periodically assayed for the specific aromatic compounds by the closed-loop stripping technique, gas chromatography, and flame ionization detection (2).

Batch 2 experiment was conducted the same as Batch 1. Carbon-14-labeled 1,2-DBE was also included (~3,000 dpm/mL). Samples were periodically assayed for the halogenated compounds by the pentane extraction GC method of Henderson et al. (3).

A third series of sterile controls and bacterial cultures were prepared with CT and carbon-14 tracer, initially at 75 µg/liter, to study transformation products. An aqueous solution containing CT (1.6 mg/mL) and carbon-14 tracer (~2 µCi/mL) was added (7.5 µL) directly to each bottle before sealing. After several weeks of incubation at 25°C, the carbon-14 labelled transformation products were characterized for methanogenic batch cultures (4).

Carbon-14 activities in the three batch experiments were determined by liquid scintillation counting (5).

RESULTS: The results did not demonstrate that ethylenedibromide was transformed under anoxic conditions when nitrate is present as the electron acceptor, although some other halogenated aliphatic compounds may be transformed under anoxic conditions when nitrate is present. CT, BDCM, DBCM, and BF were the only compounds studied that were transformed in the presence of denitrifying bacteria after 8 weeks of incubation. Chlorinated benzenes, EB, NAPH, CF, 1,1,1-TCE, and 1,2-DBE were not significantly transformed in the batch cultures. The production of CO_2 from the decomposition of CT and the partial incorporation of carbon into cells (particulates) indicated removal by biotransformation, although how this was possible remains unexplained.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The study followed generally accepted scientific principles. The study procedure followed is similar to that given in OECD guideline 302B, except excess $NaNO_3$ was added to ensure anoxic conditions, rather then measuring DOC or COD. Documentation on the equipment is limited and no documentation is given on the individual batch analyses.

REFERENCES:

1. Owen, W. R., D. C. Stuckey, J. B. Healy, Jr., L. V. Young, and P. L. McCarty, 1979, Bioassay for monitoring biochemical methane potential and anaerobic toxicity. Water Res., 13:485-492.
2. Grob, K., and F. Zurcher. 1975, Stripping of trace organic substances from water—equipment and procedures. J. Chromatogr., 117:285-299.
3. Henderson, J. E., g. R. Peyton, and W. H. Glaze, 1976. A convenient liquid-liquid extraction method for the determination of halomethanes in water at the parts-per-billion level, p. 105-112. In L. H. Keith (ed.), Identification and analysis of organic pollutants in water, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan.
4. Bouwer, E. J., and P. L. McCarty, 1983. Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. Appl. Environ. Microbiol, 45:1286-1294.
5. Bell, G. G., and F. N. Hayes, 1958. Liquid scintillation counting. Pergamon Press, Inc., New York, New York.

8. REPORT NUMBER: PH-2

STUDY TYPE: Photoreactivity

STUDY TITLE: Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 296K

AUTHORS: C. J. Howard and K. M. Evenson

DATE OF REPORT: Published in The Journal of Chemical Physics, Vol. 64, No. 11, p 4303-4306, June 1, 1976.

TESTING FACILITY: Not given

STUDY NUMBER: Not given

SPONSOR: This work was supported in part by the National Bureau of Standards, Office of Air and Water Measurement.

STUDY OBJECTIVES: Measure the absolute rate constants for the reaction of OH radicals with C_2H_6 and twelve fluorine, chlorine, and bromine substituted ethane compounds

RECOGNIZED METHOD: No

GLP: Pre-GLP

TEST SUBSTANCE: All substances tested were +99% pure. The analyses were provided by the manufacturers.

CONTROLS: Not given

CONCENTRATION OF TEST SUBSTANCES: Typical concentrations were 10^9 - 10^{11} molecules/cm^3 for OH, 8 x 10^{12} - 6 x 10^{15} molecules/cm^3 for reactant molecules, and 2.6 x 10^{16} - 2.6 x 10^{17} molecules/cm^3 for helium carrier gas.

EXPOSURE PERIOD: Not applicable

TEST PROCEDURE: The apparatus was a conventional discharge-flow system in which OH radicals are generated in a helium carrier gas stream by the fast reaction of H with NO_2. The gas temperature was 296 degrees K. Hydroxyl radicals are detected with a laser magnetic resonance spectrometer.

RESULTS: The average rate constant for EDB from 19 separate measurements was: 250(18) ± 55 (10^{-15} cm^3/molecule ·s), or roughly >1 month (tropospheric life time). The tropospheric life time τ can be made directly from a rate constant k and a typical average tropospheric concentration, [OH] = 10^6 molecules/cm^3, using the formula: $\tau = 1/k$[OH]

The authors conclude that this suggests a very small fraction of the EDB released into the troposphere will reach the stratosphere. Comparisons were made to chloro-fluorocarbons with predicted lifetimes of 10 years and therefore calculated to last long enough to reach the stratosphere.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [ ]
4. not assignable [x]

REASON: Documentation is insufficient for assessment. .

REFERENCES:

1. C. J. Howard and K. M. Evenson, 1974, J. Chem. Phys., 61:1943
2. C. J. Howard and K. M. Evenson, 1976, J. Chem. Phys., 64:197.
3. N. R. Greiner, 1970, J. Chem. Phys., 53:1070.
4. R. A. Cox, R. G. Derwent, E. A. J. Eggleton, and J. E. Lovelock Private communication with Author.
5. P. J. Crutzen and I. S. A. Isaksen, submitted to J Geophys. Res

9. REPORT NUMBER: BD-5

STUDY TYPE: Ready Biodegradability, Aerobic and Anaerobic Transformation in Soil

STUDY TITLE: Persistence of 1,2-Dibromoethane in Soils: Entrapment in Intraparticle Micropores

AUTHORS: S. M. Steinberg, J. J. Pignatello, and B. L. Sawhney

DATE OF REPORT: Published in Environ. Sci. Technol., Vol. 21, No.12, 1987.

TESTING FACILITY: The Connecticut Agricultural Experiment Station, New Haven, Connecticut 06504-1106

STUDY NUMBER: Not given

SPONSOR: Not given.

STUDY OBJECTIVES: Examine the persistence of EDB from surface soils as a source of groundwater contamination.

This report describes the desorption and bioavailability of residual EDB from Fumigated soils (referred to a "native" EDB) compared with added ^{14}C-labelled EDB.

RECOGNIZED METHOD: No. Most closely related to OECD 307, Aerobic and Anaerobic Transformation in Soil

GLP: Pre-GLP.

TEST SUBSTANCE: [1,2-^{14}C]EDB (98% purity, 23 mCi/mmol) and EDB 99% pure.

OTHER MATERIALS:

Soils: Cheshire fine sandy loam was obtained from a plot that was fumigated once at about 70 kg/ha in July 1985 by injection of EDB at a depth of 15 cm and 25 cm apart in a grid. Samples of two other soils were collected from former tobacco farms where EDB was presumed to have been applied to these fields according to standard agricultural practices at the rate of 70 kg/ha (frequency and total quantity applied are unknown). EDB use one site was halted in 1983, whereas the last known application to other site occurred in 1973. Samples collected were from 0 to 20 cm below the surface.

CONCENTRATION OF TEST SUBSTANCES: Test substance varied depending on the experiment (see test procedure below).

TEST PROCEDURE: EDB residues in the soil were extracted with methanol and then transferred to hexane after dilution of the extract with water. The hexane layer was analyzed by gas chromatography (GC). EDB in some extracts was verified by GC/MS (1).

The amount of EDB volatilized from the soil was measured using dry N_2 gas. EDB determined by GC. The soil was then extracted with methanol and analyzed for the remaining EDB.

The soild/water partition coefficients (K_p) were determined, and the concentration of sorbed EDB was calculated from the difference between added and supernatant counts. K_p was determined from the slope of linear plots of sorbed vs aqueous EDB concentrations. The apparent K_p for native EDB was determined under the same conditions.

The octanol-water partition coefficient were also measured.

The release of EDB into aqueous solution was measured using the purge technique and [^{14}C]EDB. Purging was performed for 10-minute periods, after which time gas flow was stopped, and the hexane traps were changed. An aliquot of the hexane was added to 10 mL of scintillation fluid, and amount of radioactive EDB removed was determined.

Batch methods were utilized to determine the amount of EDB released from soil into aqueous solution, and at different temperatures. Soil suspensions were prepared. Checks at 25 and 75 degrees C showed that gentle agitation had no effect on release over the time periods used.

Desorption rate and volatilization losses were also measured.

Biodegradation experiments were conducted using [^{14}C]EDB. Samples used as controls contained NaN_3 as biocide. Total EDB was determined by GC analysis of the hexane layer. [^{14}C]EDB was determined by scintillation counting. The difference between the total EDB and [^{14}C]EDB represented the native EDB which was not degraded.

The remaining methanol-extracted soil from each time point was further treated to determine the amount of fixed ^{14}C or the amount of [^{14}C]EDB converted into cellular materials. Two additional replicates at each time point were examined for amount of evolved $^{14}CO_2$.

RESULTS: Native EDB becomes entrapped in such a manner that it does not dissipate or become degraded. It is also essentially non-volatile and vigorous conditions are needed to extract EDB from environmental samples. The time from last known fumigation to sampling ranged from 0.9 to 13 years for the 3 agricultural sites. The amount of EDB determined as 27 ng/g (at 13 yrs) to 130 ng/g (at 0.9 yrs). The results indicate that EDB is not readily mobilized or degraded in the field.

The native EDB is also essentially nonvolatile. Air-drying soil samples in a Buchner funnel under aspirator suction for 24 hours did not decrease EDB concentrations.

Release of native EDB into aqueous solution from soil suspensions by purging with N_2 gas showed that EDB was removed much more quickly from fresh soil samples compared to native EDB soil samples. Purging for 100 minutes removed the freshly added EDB completely while less than 5% of the native EDB was removed. An examination of particle size of soil samples demonstrated little impact upon EDB release.

Not only is the native EDB released slowly, but also it is not readily available for degradation by soil microbes. The aerobic degradation of a freshly added spike of [^{14}C]EDB compared to that of native EDB in two demonstrated essentially no degradation of the native EDB occurred in either soil.

Mechanical breakup of the soil particles in a ball mill resulted in accelerated release of EDB. The amount of EDB released from soil during a 15-minute extraction with water increased with time of pulverization from <0.1% before pulverization to >30% after pulverization for 10 minutes. Pulverization also accelerated release into the vapor phase; the release of EDB was 40% from a sample pulverized for 5 min. compared to 8% from an unpulverized sample in a stream of N_2.

EDB in fumigated soils is extremely resistant to volatilization, release into aqueous solution, and degradation by indigenous soil microbes. Pulverization promoted release, both to the aqueous and the gaseous phases. The results suggest that EDB is entrapped in soil micropores. The authors conclude that the non-degraded portion which is sorbed into soil particles may be important because it can slowly leach out over years and result in groundwater with concentrations of 0.1 ppb or less.

DATA QUALITY: The study was carried out according to generally accepted scientific principles. Adequate information is documented that provides confidence in the results.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The study is reasonably well documented and follows generally accepted scientific principles. The results are acceptable for assessment.

REFERENCES:

1. Sawhney, B. L. , Pignatello, J. J., and Steinberg, S. M., J. Environ. Qual (See report BD-5).
2. Mingelgrin, U., Gerstl, Z., J. Environ. Qual., 1983, 12, 1.
3. Karickhoff, S. W., J Hydraul. Eng., 1984, 110, 707.
4. Crank, J., The Mathematics of Diffusion, 2nd ed., Glarendon: Oxford 1975.
5. Cooney, D. O., Adesanya, B. A., Hines, A. L., Chem. Eng. Sci., 1983, 38, 1535.
6. Pignatello, J. J., Appl. Environ. Microbiol., 1986, 51, 588.

10. REPORT NUMBER: HY-2

STUDY TYPE: Ready Biodegradability; hydrolysis

STUDY TITLE: Reaction Products and Rates of Disappearance of Simple Bromoalkanes, 1,2-Dibromopropane, and 1,2-Dibromoethane in Water.

AUTHORS: Timothy M. Vogel and Martin Reinhard.

DATE of REPORT: Published in Environmental Science Technology, Vol. 20, No. 10, pp992 – 997, 1966.

TESTING FACILITY: Environmental Engineering and Science, Civil Engineering Department, Stanford University, Stanford, CA 94305

STUDY NUMBER: Not given

SPONSOR: Support for this work was provided by the U. S. EPA through the Office of Research and Development, Grant EPA–R-808034-010, and the R. S. Kerr Environmental Research Laboratory, EPA-R-808851.

STUDY OBJECTIVES: This study reports on the reactivity of some mono- and dibromo-alkanes in aqueous buffers. Hydrolysis and elimination reactions were considered. The available data on the reactivity of alkyl bromides in water were analyzed with respect to Taft's linear free energy relationship (LFER).

RECOGNIZED METHOD: No. Comparable to OECD guideline 111 for hydrolysis.

GLP: Pre-GLP.

TEST SUBSTANCE: 1,2-DBP, 1,2,3-tribromopropane (1,2,3-TBP), 1,3-DPB, EDB, 1-bromo-3-phenylpropane (BPP), and 1-bromo-n-heptane (BH). They were the highest purity available and used as received.

Stock solutions of the organics were prepared in methanol. Pentane was used as the extractant.

OTHER MATERIALS: Reagents for the buffer solutions were obtained from Baker Chemical Company. Solutions were adjusted to the correct pH at the reaction temperature with either dilute HCl or NaOH. The ionic strength of the final solutions was 0.1 M. The pH was measured at the experimental temperature by using a glass electrode.

CONTROLS: An internal standard (IS) was added to the pentane before extraction. 1,3-DBP was used as the IS For 1,2-DBP, and vice versa. Tetrachloroethylene was used as the IS for EDB. Mass spectra were compared with spectra from the National Bureau of Standards library for product identification.

CONCENTRATIONS OF TEST SUBSTANCES: Not given

EQUIPMENT: An electron capture detector (ECD) was used for 1,2-DBP, 1,3-DBP, and EDB, and a flame ionization detector (FID) was used for BH and BPP. Peak-area integration was carried out with a Model 4000 data system (Spectra Physics). Pentane-extractable reaction products were analyzed by GC/MS.

TEST PROCEDURE: The kinetic experiments were performed in flame-sealed glass ampules. Ten milliliters of each buffer solution was pipetted into glass ampules, which were subsequently spiked with the alkyl bromide solution (10mg/l) and immediately sealed with a propane flame. The ampules were immersed in a temperature-controlled water bath, the rates studied in the 45 - 90°C temperature range, and removed at pre-selected time intervals after the start of the experiment. These were added to volumetric flasks containing pentane, stoppered tightly and shaken vigorously by hand for 3 minutes.

Two microliters of the pentane extract was injected onto a 15-m Durabond DB-5 thick-film capillary column using a 200°C Grob injector and quantified. Quantification was based upon peak-area integration with a Model 4000 data system. The internal standard was added to the pentane before extraction.

Pentane-extractable reaction products were analyzed by GC/MS for product identification.

The fraction of an organic in the gas phase was estimated from its Henry's constant, H, the liquid-phase volume and vapor-phase volume (1). H was estimated from vapor pressure and solubility data (2). The 20 degree C H constants of the compounds evaluated ranged from 0.25 atm·L/mol for 1,3-DBP to 6.6 atm·L/mol for BH. The vapor to liquid ratios at 20 degrees C were estimated to range form 1×10^{-4} for 1,3-DBP to 3×10^{-3} for BH. Such small gaseous fraction (<0.3%) would not normally affect the determination of aqueous reaction rates. However, Munz (3) found that H increased by a factor of approximately 2 for a 15 degree C temperature increase within the range 10 – 30 degrees C. Assuming the H doubles every 15 degrees C over the entire temperature range (20 – 95 degrees C), H at 95 degrees C increases by a factor of 32. Hence, the gas to liquid ratio of BH at 50°C would be ~1% and at 95°C, it would increase to ~10%. This estimation was taken into account, particularly for compounds with a very low water solubility such as BH.

RESULTS: BPP and BH reacted to the corresponding alcohols with no elimination products detected by pentane extraction and GC/MS. EDB, 1,2-DBP, and 1,2,3-TBP reacted to form various bromoalkene isomers: EDB yielded vinyl bromide. Dehydrobromination has been reported to be the major transformation for DBCP in buffered aqueous solutions (1).

Pseudo-first order reaction (i.e., disappearance) rates were observed. In general, all disappearance rates were pH-independent at a pH range of 7 – 9. The reaction rates and half-lives extrapolated to 25 degrees C were calculated by using the Arrhenius relationship. From this is was determined that the half-life for EDB was 2.5 years.
In general the estimated half-lives of alkyl bromides increased with degree of halogenation. The data evaluated by linear free energy relationships indicate a general decrease in reactivity, i.e., an increase in half-lives, with increase in the inductive constant. Any attempt to correlate the data presented to groundwater conditions should be made with caution because study conditions used solutions of relatively high ionic strength (0.1 M), higher than what is typical for fresh waters (<0.01M) (5), and at temperatures 20-70°C above typical environmental temperatures.

STATISTICAL METHODS: The Arrhenius equation was used to extrapolate the reaction rate constant measured at elevated temperatures to 95 degrees C. The statistical uncertainties of the activation energy and observed first order rate constant of overall hydrolysis at 25 degrees C were estimated according to procedures of Lindren (6).

DATA QUALITY: The study examines the disappearance of specific halogenated aliphatic compounds from the enviornment based upon an evaluation of certain physical chemical parameters. The study results may be useful by helping to explain environmental fate findings from other studies. Based upon this determination alone a specific reliability rating for this study cannot be assigned, but in no way reflects upon the scientific merits of this study in the proper context.

RELIABILITY:

5. w/o restriction [ ]
6. w restriction [ ]
7. not reliable [ ]
8. not assignable [x]

REASON: Study is more properly assigned to research then it is to a specific environmental fate protocol.

REFERENCES:

1. Burlinson, N. E.; Lee, L. A.; Rosenblatt, D. H., *Environ. Sci. Technol.*, 1982, 16,627-632.
2. Thomas, R. G., In Handbook of Chemical Property Estimation Hanbook; :Lyman. W. J.; Reehl, W. F.; Rosenblatt, D. H., Eds.; McGraw-Hill: New York, Ny 1982; pp 15-1 - 15-34.
3. Munz, C., *Ph. D. Dissertation*, Stanford University, Stanford, CA, 1985
4. Mabey, W. R., Barich, V, Mill, T., *Proceedings of the Division of Environmental Chemistry*, American Chemical Society, kWashington, DC, August, 1983, Preprint Extended Abstract, pp 354-356.
5. Schwarzenbach, R. P., kGiger, W., Schaffner, C., and Wanner, C. O., *Environ. Sci. Technol., 1985,19, 322-327.*
6. Lindgren, B. W., *Statistical Theory*, MacMillan, New York, NY, 1976, pp533-546.

11. REPORT NUMBER: BD-6

STUDY TYPE: Anaerobic Transformation in Methanogenic Aquifer Material

STUDY TITLE: Biotransformations of Selected Alkylbenzenes and halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study

AUTHORS: B. H. Wilson, G. B. Smith, and J. F Ross

DATE of REPORT: Published in Environmental Science Technology, Vol. 20, No. 10, pp 997-1002, 1986

TESTING FACILITY: Not given

STUDY NUMBER: Not given

SPONSOR: This study was supported by the United States Air Force through Interagency Agreement RW57930615-01-1 with the U.S. Environmental Protection Agency. The work was funded under Cooperative Agreement CR-8111146 between the R. S. Kerr Environmental Research Laboratory and the University of Oklahoma at Norman, OK.

STUDY OBJECTIVES: The behavior of two groups of commonly occurring contaminants were examined in a synthetic microcosm constructed with authentic aquifer material that receives municipal landfill leachate and is known to support methanogenesis. The alkylbenzenes studied were benzene, toluene, ethylbenzene, and o-xylene, while the halogenated aliphatic hydrocarbons studies were 1,1-dichloroethylene, *trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene, trichloroethylene and 1,2-dibromoethane.

RECOGNIZED METHOD: No. Most similar OECD test guideline is OECD 307, Aerobic and Anaerobic Transformation in Soil.

GLP: Not stated.

TEST SUBSTANCE: The chemicals used were high purity (>97%) benzene, toluene, ethylbenzene, *o*-xylene, [^{14}C]-toluene, 1,1-dichloroethylene, *trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene, trichloroethylene, and 1,2-dibromoethane.

OTHER MATERIALS: Aquifer material for the anaerobic fate studies was obtained from sites adjacent to a landfill. Solid samples were taken by digging down to the region of methanogenesis and scooping up the aquifer material

into sterilized 1-qt canning jars. The landfill was sited over highly permeable alluvium composed of silt, sand, clay, gravel, and dune sand. The depth of the alluvium varied from 1.7 to 1.22 m and lies over a 91-m layer of dense clay and chert gravel. The water table averaged from 0.6 to 1.5 m below the original land surface in areas adjacent to the river.

Liquid samples were taken by allowing the hole to fill with water and collecting the water in sterile glass containers. The aquifer water collected for the study was analyzed for metals, various parameters (pH, alkalinity, nitrate, etc.), and organic compounds.

CONTROLS: Sterile controls were autoclaved overnight at 121 degrees C prior to dosing.

CONCENTRATIONS OF TEST SUBSTANCES: Initial concentrations of EDB were 194 and 140 ug/L of pore water.

EXPOSURE PERIOD: 0, 3, 7, 16, and 40 weeks for the halogenated aliphatic hydrocarbons and 0, 6, 12, 20, 40, and 120 weeks for the alkylbenzenes.

EQUIPMENT: The analyses were conducted on a Finnigan Model 4000 GC/MS system interfaced to an INCOS data system in accordance with EPA Method 624 (1). Both studies used a Hewlett-Packard 5880A gas chromatograph with flame ionization detection with N_2 carrier gas at a 30 mL/min flow rate. The limit of detection for the alkylbenzenes and 1,2-dibromoethane was 0.1 µg/L; for the chlorinated hydrocarbons, the limit of detection was 1 µg/L.

TEST PROCEDURE: All manipulations were performed in an anaerobic glovebox to ensure the maintenance of methanogenic conditions in the aquifer material, and all equipment in contact with the aquifer material was sterilized. The aquifer material was slurried by the addition of 15% by weight aquifer water and then poured into 160-mL serum bottles, resulting in approximately 100 g of aquifer material (wet weight) in each experimental unit. The dry weight of the solids averaged 67.5g. About 2 ml of dosing solution were added to the microcosms. The microcosms were stored upside down in the dark at 17 degrees C (the average groundwater temperature of the aquifer from which it was taken).

Two to four replicates of each treatment were analyzed at each sampling interval. Bottles were sampled by purging the volatile compounds onto a trap. Analysis was done by GC/FID.

The disappearance of halogenated aliphatic hydrocarbons from the methanogenic aquifer was measured at week 0, 3, 7, 16 and 40 after introduction of initial concentrations of these materials.

RESULTS: The disappearance of 1,2-dibromoethane was quite rapid; by 7 weeks of incubation, the concentration of 1,2-dibromoethane had been reduced to 27% of the control concentrations or less. At 16 weeks of incubation, the concentrations in the living samples were below the limit of detection. Chromatograms of samples at 3 and 6 weeks indicated the appearance of a new peak coinciding with the disappearance of 1,2-dibromoethane. GC/MS analyses at 6 weeks were unable to identify this peak. Transformation of 1,2-dibromoethane was also observed in the autoclaved controls of this study with the simultaneous appearance of a new peak in the chromatograms.

All four of the alkylbenzenes disappeared in the methanogenic aquifer material, but the disappearance was not rapid; long lag times were required before significant removal of all compounds was observed. Within the first 6 weeks of incubation, toluene concentrations were reduced to 13% of the original concentrations. Benzene, ethylbenzene, and o-xylene were not significantly degraded during the first 20 weeks of incubation. At 120 weeks of incubation, the concentrations of all four compounds were reduced to less than 1% of the original concentrations in the living samples. In contrast, there was no evidence of loss of benzene, toluene, ethylbenzene, or o-xylene in the autoclaved aquifer material at the 40 week interval. By 120 weeks of incubation the concentrations in the autoclaved samples for benzene, toluene, ethylbenzene, and o-xylene were 70%, 67%, 73%, and 66% of the original concentrations, respectively. Presumptive evidence of biological transformation of all four alkylbenzenes was based on extensive removal of material in living samples compared to autoclaved controls.

DATA QUALITY: This study is reasonably well documented, had adequate control samples, and meets generally accepted scientific principles. It was not stated whether or not GLP procedures were followed.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASON: The study was reasonably well documented and meets generally accepted scientific principles. More complete daily documentation on the various parameters would improve the quality. However, recognizing that this is a published report of laboratory findings it is understood that such data are omitted from printing because of costs.

REFERENCES:

1. U. S. Environmental Protection Agency In *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater;* Longbottom, J. E.; Lichtenberg, J.J., Eds.; U. S. Governmental Printing Office: Washington, DC; Purgeable Method 624, pp 624-1-624-12; EPA-600/4-82-057.

12. REPORT NUMBER: BD-7

STUDY TYPE: Enzyme purification methodology

STUDY TITLE: Purification and characterization of a bacterial dehalogenase with activity toward halogenated alkanes, alcohols and ethers

AUTHORS: Janssen, D. B. et.al.

DATE of REPORT: Published in *Eur. J. Biochem.*, 171, 67-72, 1988.

TESTING FACILITY: Not given.

STUDY NUMBER: Not given

SPONSOR: Not stated.

STUDY OBJECTIVES: Purification of a dehalogenase from bacteria strain GJ70, a gram-positive actinomycete-like organism (previously identified as Acinetobacter) isolated from activated sludge.

RECOGNIZED METHOD: No. Most comparable to OECD guideline 302, Inherent Biodegradability.

GLP: Not applicable

TEST SUBSTANCE: The dehalogenase was isolated from strain GJ70 grown to a density of 1mg/ml; cultivating conditions were: pH 7, 30 degrees C and 70% oxygen. These cells were harvested in a continuous centrifuge. Aliphatic dehalogenase was purified from crude extract dehalogenase from Xantobacter. Molecular weight and amino acid sequence were determined for the native and purified enzyme.

CONTROLS: Not applicable

CONCENTRATIONS OF TEST SUBSTANCES: Not applicable

TEST PROCEDURE: Aliphatic dehalogenase,purified from crude extract dehalogenase from Xantobacter, was examined for enzyme activity using 1-bromopropane as substrate. One unit of enzyme defined as the activity that catalyzes the formation of 1 umol halide/minute. Dehalogenase activity was determined at 30 degrees C and pH 8.8 in suitable buffer and substrate. Michaelis-Menten constants were determined from halide production curves. V_{max} values were calculated from Lineweaver-Burke plots, and K_m values derived from the same plot. The activity of the purified enzyme was measured against a broad range of brominated, chlorinated and iodomated compounds.

RESULTS: EDB was rapidly hydrolyzed by the dehalogenase, with the highest rate, expressed as a percent of the rate of the standard, 1-bromopropane. The rate was 172%. This paper covers that purification of a dehalogenase isolated from strain GJ70. The relationship to EDB is the fact that there are microbes in the environment that have the ability to remove halogens from alkanes, alcohols, and ethers. It was proposed as potential mechanism for enzyme-catalyzed hydrolytic dehalogenation, demonstrating that EDB in the environment may be subject to biodegradation by microorganisms.

DATA QUALITY: Scientific research presented relating to the isolation, identification, and activity of a microbial enzyme with potential to degrade a wide variety of environmental contaminants. The study results may be useful by helping to explain environmental fate findings from other studies. Based upon this determination alone a specific reliability rating for this study cannot be assigned, but in no way reflects upon the scientific merits of this study in the proper context.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [ ]
4. not assignable [x]

REASON: Paper is a summary of research findings pertinent to a specific enzyme capable of biodegradation of environmental contaminants. Study is more properly assigned to research then it is to a specific environmental fate protocol.

REFERENCES: None.

13. REPORT NUMBER: BD-8

STUDY TYPE: Aerobic transformation in soil

STUDY TITLE: Ethylene Dibromide Mineralization in Soils under Aerobic Conditions

AUTHORS: J. J. Pignatello

DATE of REPORT: Published in *Applied and Environmental Microbiology*, p 588-592, March, 1986.

TESTING FACILITY: Department of Soil and Water, Connecticut Agricultural Experiment Station, New Haven, Connecticut 06504

STUDY NUMBER: Not given

SPONSOR: Supported by funds from the Connecticut Agricultural Experiment Station.

STUDY OBJECTIVES: This report reexamines biodegradation of EDB by soil microorganisms.

RECOGNIZED METHOD: No. Comparable to OECD guideline 307, Aerobic Transformation in Soil.

GLP: Pre-GLP.

TEST SUBSTANCE: 1,2-dibromoethane (ethylene dibromide, EDB); Purity: not given.
[1,2-^{14}C]EDB (23 mCi/mmol; 98% radiochemical purity) was obtained from New England Nuclear Corp., Boston, Massachusetts.

OTHER MATERIALS: Samples were collected from a site that overlies an aquifer (10 to 20 m of sandy soil above bedrock), which discharges into a shallow stream. The stream and several test and production wells had been contaminated with EDB in the range of 0.1 to 11 µg/L for at least 1 year prior to sampling for this study.

Sampled sites collected represent extremes of organic compound content and microbial activity. The first soil sample (S1) was composed of organic carbon-poor (0.24% organic carbon), medium-to-coarse sand taken from a

streambed which was aerobic in its native state. Experiments were conducted with a 3:2 mixture (dry wt/vol) of solid material and accompanying stream water. The second soil sample (S2) was composed of organic carbon-rich (14% organic carbon), muddy soil from an area partially anaerobic in its native state. Levels of EDB in this site were 4.2 and 8.6 µg per kg.

CONTROLS Autoclaved controls of S1, S2, stream water, and distilled water were run concurrently.

CONCENTRATIONS OF TEST SUBSTANCES: Incubations were carried out at either 6 to 8 ppb (µg/L) or 15 to 18 ppm (mg/L) of EDB.

EXPOSURE PERIOD: Exposure times varied from 0 to 35 weeks.

TEST PROCEDURE: S1 and S2 were added to flasks, leaving 75 mL of headspace, and 129 mL of headspace, respectively. Flasks were spiked with stock EDB, prepared in autoclaved distilled water, and incubated inverted 23 ± 1 degrees C. The large headspace in the flasks served as a reservoir for oxygen and was monitored in a separate identical flask preparatio. Actual O_2 levels in the experimental flasks were not measured. S1 flasks remained aerobic throughout the longest incubations (99 days), but oxygen in S2 flasks dropped by 90% after 7 weeks. Oxygen in S2 flasks was replenished by a flow of 1 headspace volume of air through a needle; displaced EDB was measured by sampling before and after this operation. Sulfate and nitrate levels persisted throughout the study period, evidence that aerobic conditions were maintained. Sulfate and nitrate disappeared from other flasks deliberately made anaerobic by sparging. Periodically, after brief shaking, subsamples were withdrawn.

S2 was suspended in distilled water spiked with [1,2-^{14}C]EDB (60 ug EDB/liter) and carbon product fractionation performed. The headspace was sufficient to keep the culture aerated for the 13 days of the experiment.

A replicate vial was taken periodically, and samples were assayed for radioactivity and EDB concentration. A purge train described by Bouwer and McCarty (1) comprised of a Tenax column trap, a pair of CO_2 traps, a heated stainless steel coil, a second pair of CO_2 traps. The purged culture was extracted with hexane and then filtered. The solids were combusted in a biological oxidizer and the $^{14}CO_2$ was collected in trap/scintillation fluid. Recovery with this instrument and [^{14}C]sucrose standards was 96.4 ± 0.8. Production of $^{14}CO_2$ by soil microbes was confirmed.

The method of Barnhart and Vestal (3) for measuring the extent of acetate incorporation into microbial lipids was used to assess EDB inhibition of microbial activity. S1or S2 was spiked with EDB in distilled water and incubated at 25 degrees C for either 3 or 12 hours. The initial EDB concentrations were 0, 0.1, 1, 10, 50, 100, and 1,000 ppm.

RESULTS: Aerobic degradation: EDB was almost completely degraded within 1 week in both S1 and S2 at initial concentrations of 6 to 8 µg/Liter. At termination of this study, the flasks were charged with hexane to extract EDB from the entire contents, including the headspace. GC analysis for EDB revealed it was near or below the detection limit of 0.02 µg/L, representing at least 99% removal.

The results of soil incubations at 15 to 18 ppm demonstrated that soil components can catalyze EDB hydrolysis or chemically react with EDB.

Carbon products were determined by incubating diluted S2 suspensions with [^{14}C]EDB. Nearly all of the recovered ^{14}C in active cultures was associated with unreacted EDB, CO_2, or unextractable forms in filterable solids. The^{14}C as CO_2 and solids increased with increasing EDB removal. Recovered EDB accounted for virtually all of the ^{14}C trapped by Tenax and extracted from the culture by hexane and ether.

The ^{14}C bound to solids represents carbon metabolized into cell materials and paralleled the extent of $^{14}CO_2$ evolution. A small fraction of the bound ^{14}C resulted from abiotic processes. A small percentage of initial ^{14}C which non-extracted appears to include products of both biotic and abiotic reactions, consisting of metabolic intermediates of EDB and water soluble EDB hydrolysis products such as 2-bromoethanol and ethylene glycol.

TABLE 1. Carbon product fractionation of [^{14}C]EDB in soil (S2) under aerobic conditions

Replicate (R) or autoclaved control (C) no.	Incubation Time (days)	%EDB remaining (gas chromato-graphic assay)[a]	EDB in Trays And extracts	% Initial ^{14}C recovered as[a] CO_2	Tenax-trapped organic compounds[b]	Hexane-extracted organic compounds[b]	Ether-extracted organic compounds[b]	Highly volatile organic compounds	Unextract-able ^{14}C in culture filtrate	Unextract-able ^{14}C in bound to solids	Total ^{14}C Recovered (%)
R1	5.7	54 ± 5	47 ± 5	20 ± 1	1 ± 3	1 ± 1	0.0	1.4 ± 0.1	3.9 ± 0.1	17 ± 1	90 ± 3
R2	8.8	29 ± 3	28 ± 3	33 ± 1	1 ± 2	0.3 ± 0.6	0.0	0.8 ± 0.7	3.6 ± 0.1	26 ± 2	93 ± 3
R3	13	17 ± 2	14 ± 2	41 ± 1	2 ± 1	0.1 ± 0.4	0.0	0.6 ± 0.1	6.9 ± 0.2	23 ± 1	87 ± 2
R4	13	6 ± 1	6 ± 1	45 ± 1	0.1 ± 0.5	0.3 ± 0.3	0.1 ± 0.1	0.3 ± 0.1	4.1 ± 0.1	33 ± 2	89 ± 3
C1	13	91 ± 8	93 ± 10	0.6 ± 0.4	0 ± 1	0.0	0.0	0.8 ± 0.3	1.9 ± 0.1	2.6 ± 0.2	93 ± 3
C2	13	91 ± 8	92 ± 9	0.2 ± 0.3	6 ± 5	0.0	0.0	0.7 ± 0.3	2.0 ± 0.1	2.7 ± 0.2	100 ± 4

[a] Uncertainty given as ± 1 standard deviation
[b] Other than EDB.

Soil aerobes or aerobic consortia may use EDB as a source of carbon and energy. Approximately equal amounts of EDB are converted to CO_2 and cellular carbon. Degradation at ppb levels was rapid and complete, whilst degradation at ppm levels was slow. EDB loss and bromide ion appearance and irreversible incorporation of ^{14}C into soil particles of sterile controls indicate soil-mediated chemical mechanisms of EDB destruction also.

STATISTICAL METHODS: Standard derivations were calculated.

DATA QUALITY: The study was reasonably well documented and meets generally accepted scientific principles. The results are useable for assessment of the environmental degradation under aerobic and anaerobic conditions.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [x]
3. not reliable [ ]
4. not assignable [ ]

REASONS: Although the study is reasonably well documented and meets generally accepted scientific principles, one would have like more documentation on various experimental parameters, such as, daily temperature, sample recovery, etc..

REFERENCES:

1. Bouwer, E. J. and P. L. McCarty, 1983, Transformations of halogenated organic compounds under denitrification conditions. *Appl. Environ. Microbiol.* 45:1295-1299.
2. Bouwer, E. J. and P. L. McCarty, 1983, Transformations of halogenated organic compounds under denitrification conditions. *Appl. Environ. Microbiol.* 45:1286-1294.
3. Barnhar, C. L. H., and J. R. Vestal. 1983. Effects of environmental toxicants on metabolic activity of natural microbial communities. *Appl. Environ. Microbiol.* 46:970-977.
4. Leo, A., C. Hansch, and D. Elkins, 1971. Partition coefficients and their uses. *Chem. Rev.*, 71:525-554.
5. Lyman, W. J., 1982, Octanol/water partition coefficient, p. 1-1 to 1-54, *In* W. J. Lyman, W. F. Reehl (ed.), Handbook of chemical property estimation methods environmental behavior of organic compounds. McGraw-Hill Book Co., New York.
6. Roger, R. D., and J. C. McFarlane. 1981. Sorption of carbon tetrachloride, ethylene dibromide, and trichloroethylene on soil and clay. *Envion. Monit. Assess.* 1:155-162.
7. Schwarzenback, R. P., W. Gger, C. Schaffner, and O. Wagner. 1985. groundwater contamination by volatile halogenated alkanes: abiotic formatio of volatile sulfur compounds under anaerobic conditions. *Envion. Sci. Technol.* 19:322-327.

14. REPORT NUMBER: MOD-2

STUDY TYPE: Modeling (bioconcentration)

STUDY TITLE: Predicted Bioconcentration Factors and Soil Sorption Coefficients of Pesticides and Other Chemical

AUTHORS: Eugene E. Kenaga

DATE of REPORT: Published in *Ecotoxicology and Environmental Safety*, 4, 26-28, 1980.

TESTING FACILITY: Not given

STUDY NUMBER: Not given

SPONSOR: Not applicable

STUDY OBJECTIVES: To predict (through modeling) soil sorption coefficients and bioconcentration factors for compounds where these values are not known but water solubility is known.

RECOGNIZED METHOD: No

GLP: Not applicable

TEST SUBSTANCE: Not applicable

OTHER MATERIALS: Not applicable

CONCENTRATIONS OF TEST SUBSTANCES: Not applicable

EXPOSURE PERIOD: Not applicable

EQUIPMENT: Not applicable

TEST PROCEDURE: This report uses certain equations developed by Kenaga and Goring to predict soil sorption coefficients and bioconcentration factors for compounds where these values are not known but water solubility is known.

The equations used in this study, taken from Kenaga and Goring (1) are shown below.

a. Log BCF* = 2.791 – 0.564 (log WS) ± 1.99 orders of magnitude (OM) (95% confidence limit) from the calculated value. WS units are ppm.
b. Log BCF* = -1.576 + 1.119(log K_{oc}) ± 1.95 OM (95% confidence limit) from the calculated value.

*BCF values are calculated from equations for flowing water systems (f) rather than from the terrestrial-aquatic systems (t) shown by Kenaga and Goring (1978). BCF (f) value average almost one order of magnitude higher than BCF(t) values. The equation used for prediction of soil sorption coefficient values was as follows:

c. Log K_{oc} = 3.64 – 0.55 (log WS) ± 1.23 OM (95% confidence limits) from calculated value.

Water solubility data were obtained from the summaries of Kenaga and Goring (1) and the *Pesticide Manual* of Martin and Worthing (2). Soil sorption data were obtained from the summary of Kenaga and Goring (3). Two predictive values for BCF (derived from WS and K_{os} equations) were given for comparative purposes.

The validity of these equations was questioned for use with compounds that do not penetrate tissue, are rapidly degraded or rapidly lost from soil or water, are rapidly metabolized by living organisms, or are ionic and bound strongly to soil by electrostatic interaction. Exceptions and limitations in the use of these equations for predictive purposes were addressed.

RESULTS: The predicted and experimental values of BCF and K_{oc} from water solubilities were listed. The 100 experimental values of K_{oc} were compared with calculated K_{oc} values. 87% were one order of magnitude and 95% were two orders between the values. Compounds having a K_{oc} value of around 1000 are quite tightly bound to organic matter in soil and are considered immobile. Those below 100 are moderately to highly mobile. The authors illustrate that the K_{oc} value is useful as an indicator of the potential leachability of compounds through soil or their potential binding on stream sediments. K_{oc} may also indicate whether compounds applied to land are more likely to enter water by runoff in solution or on eroded solids.

TABLE 1. Water Solubility, Soil Adsorption Coefficient, and Bioconcentration Factor Data: Experimental and Calculated

Chemical (use)	Water solubility[a] (ppm)	Soil Adsorption Coefficient		Bioconcentration factor predicted from[b]		Bioconcentration factor[a]
		K_{oc}[a]	K_{oc}[b]	WS	K_{oc}	
...	...	...	...	...	...	...
Ethylene dibromide (IF)[c]	3,370	44	50	6	2	
...	...	...	...	...	...	...

[a] Experimental values (as summarized by Kenaga and Goring, 1978).
[b] Calculated values (using equation of Kenaga and Goring, 1978).
[c] (IF) insecticide fumigant.

STATISTICAL METHODS: Not applicable

DATA QUALITY: The report is an examination of a model that may have utility in examining the environmental transport of pesticides using pre-selected parameters. No attempt is made to examine the scientific quality since this was designed as a tool to help in an initial or early assessment of potential for a chemical to partition into soil and animal tissue. Most preliminary comparisons must be confirmed with experimental results.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [ ]
4. not assignable [x]

REASON: Kenaga values have been used in exposure assessment, but only as the last resort. The calculated results should only be used if actual laboratory or field data are not available. The use of these results may be invalid for compounds that have certain characteristics/properties which they have identified in their report.

REFERENCES:

1. Reference not given in paper
2. Martin, H. and Worthing, C.R., (1977), *Pesticide Manual* 5th ed. British Crop Protection Council, Worcestershire, England.
3. Kenega, E. E., and Goring, C. A. I. (1980). *Relationship Between Water Solubility, Soil Sorption, Octanol-Water partitioning, and Bioconcentration of Chemicals in Biota.* In Aquatic Toxicology ASTM STP 707, (J. C. Eaton, P. R. Parrish, and A. C. Hendricks, Eds.), American Society for Testing and Materials, in press. (In the paper the reference indicates Kenega and Goring 1978)

15. REPORT NUMBER: BD-9

STUDY TYPE: Aerobic Soil Metabolism

STUDY TITLE: Adaptation to and Biodegradation of Xenobiotic Compounds by Microbial Communities from a Pristine Aquifer

AUTHORS: C. M. Aelion, C. M. Swindoll and F. K. Pfaender

DATE of REPORT: Published in Applied and Environmental Microbiology, p 2212-2217, Sept, 1987.

TESTING FACILITY: Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, NC 27514

STUDY NUMBER: Not given.

SPONSOR: This research was supported by the Environmental Protection Agency under cooperative agreement CR-811828.

STUDY OBJECTIVES: The objectives of this research were to examine the ability of a subsurface microbial community previously exposed to no known pollutants to degrade a wide variety of Xenobiotic compounds, determine rates of degradation, and identify patterns of degradation.

RECOGNIZED METHOD: No. Comparable to OECD guideline 307, Aerobic and Anaerobic Transformation in Soil

GLP: Not stated, although it is well established that this particular testing facility has complied with GLP regulations and principles since they were promulgated.

TEST SUBSTANCE: The radiolabelled substrates used included: *m*-[U-^{14}C]cresol, [U-^{14}C]ethylene dibromide, [U-^{14}C]phenol, *m*-[U-^{14}C]aminophenol, [U-^{14}C]chlorobenzene, [U-^{14}C]1,2,4-trichlorobenzene, *p*-[U-^{14}C]chlorophenol, *p*-[U-^{14}C]nitrophenol, [U-^{14}C]aniline hydrochloride and [U-^{14}C]barium carbonate. Purity: Not given.

OTHER MATERIALS: Aquifer solid samples were aseptically taken from an uncontaminated aquifer site, in unconsolidated material from the margin of the flood plain of a small river near. Uniform fine sand from the saturated zone of the profile was used in all experiments. This area of the profile, at a depth of 4.5 to 5.6 m below the surface, was under artesian head. There was approximately 0.22 mL of pore water per g of soil in this layer of the aquifer.

CONTROLS: Sodium azide was added as a metabolic inhibitor.

CONCENTRATIONS OF TEST SUBSTANCES: Two concentrations were used, approximately 10 to 50 and 500 to 1,000 ng/g of soil.

EXPOSURE PERIOD: Varied

EQUIPMENT: The amount of activity recovered (disintegrations per minute) was determined by using a Packard Tri-Carb 300D liquid scintillation counter.

TEST PROCEDURE: To evaluate the rates of mineralization by the microbial community, $^{14}CO_2$ evolution from a number of radiolabelled compounds was monitored over time. Because the microbes originated from aquifer solids, concentrations are presented on a solids dry weight basis. It should be recognized however, that all incubation vials contained approximately 1 g of aquifer solids and 24 mL of sterile distilled water; thus the microorganisms were in a more dilute suspension than the concentrations reflect.

Aquifer material was placed in a blender with aerated sterile distilled water, and a slurry was made. Sodium azide was added as a metabolic inhibitor. The radiolabelled isotope was added to all of the vials, and the remaining volume was filled with sterile distilled water. The headspace-free vials were inverted during incubations, carried out in the dark at 17 degrees C.

Samples were taken at specific time intervals of replicate samples and controls. The samples were then acidified with phosphoric acid to pH 2, and a center well containing 0.15 mL of 1 N KOH was placed in the vial headspace. The vials were placed on a rotary shaker at 80 rpm for approximately 18 hours, during which the $^{14}CO_2$ was trapped in the base. The amount of activity recovered (DPM) was determined by using a liquid scintillation counter. The efficiency of this method for trapping $^{14}CO_2$ was determined. An increase in the rates of mineralization (as a function of degradation) of radiolabeled substrates with exposure was used as an indication of adaptation.

Enumeration of specific degraders was based on the most-probable-number (MPN) technique (3) as modified by Somerville et al. (4). Two sets of MPNs were set up to assess changes in the numbers of degraders during adaptation; one set before adaptation, and the second set to assess the MPN after adaptation. After adaptation had been observed in the respiration experiment (day 35), radiolabelled *p*-nitrophenol (100 ng per vial) was added to all of the vials, which were allowed to incubate for an additional 26 days.

Replicate samples were scored positive if the $^{14}CO_2$ disintegrations per minute produced were greater than or equal to 3 times the control values for that dilution series. The MPN values were then calculated from these data by using the computer program of Clarke and Owens (5).

RESULTS: The aquifer microbial community (solids) was capable of degrading a wide variety of xenobiotic compounds. The time frame of degradation varied from days for phenol, *p*-chlorophenol, and EDB, to weeks or months for *m*-cresol, *m*-aminophenol, aniline, and *p*-nitrophenol, and to years for the chlorinated benzenes.

EDB displayed a rapid rate of mineralization, initially, which leveled off such that a maximum percent respired was reached within weeks (@20-25%). Initial degradation rates were calculated by linear regression. The rate for EDB was 1.0% per day. A slightly greater percent of EDB was mineralized at the lower concentrations. The community was apparently already adapted to the utilization of EDB since no adaptation period was required before significant degradation occurred. No attempt was made, however, to identify the steps involved in the adaptation process.

DATA QUALITY: Although the study appears to be carried out according generally accepted scientific principles, it is not possible to apply the results obtained from one aquifer to other aquifers without additional confirmatory data. The data suggest that there may be naturally occurring microorganisms in aquifer soils that could metabolize EDB.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [ ]
4. not assignable [x]

REASON: Documentation insufficient for assessment.

REFERENCES:

1. Dunlap, W. J., J. F. McNabb, M. R. Scalf, and R. L. Cosby, 1977. Sampling for organic chemicals and microorganisms in the subsurface. Publication no. EPA-600/2-77-176. Government Printing Office, Washington, D. C.
2. Wilson, J. T., J. F. McNabb, D. L. Balkwill, and W. C. Ghiorse. 1983. Enumeration and characterization of bacteria indigenous to a shallow water-table aquifer. *Ground Water*. 21:134-142.
3. Lehmicke, L. G., R. T. Williams, and R. L. Crawford. 1979. ^{14}C-most-probable-number method for enumeration of active heterotrophic microorganisms in natural waters. *Appl. Environ. Microbiol.* 38:644-649..
4. Somerville, C. C., C. A. Monti, and J. C. Spanin. 1985. Modification of the ^{14}C-most-probable-number method for use with nonpolar and volatile substrates. *Appl. Environ. Microbiol.* 49:711-713.
5. Clarke, K. R., and N. J. P. Owens. 1983. a simple and versatile micro-computer program for the determination of 'most probable number'. *J. Microbiol. Methods* 1:133-137.

16. REPORT NUMBER: BD-10

STUDY TYPE: Transformation under methanogenic conditions.

STUDY TITLE: Ethylene Dibromide Transformation under Methanogenic Conditions

AUTHORS: Edward J. Bouwer and Perry L. McCarty

DATE of REPORT: Published in *Applied and Environmental Microbiology*, p 527-528, Aug. 1985.

TESTING FACILITY: Not given.

STUDY NUMBER: Not given.

SPONSOR: This research was supported in part by grant EPA-R-80803410 from the Office of Research and Development, U. S. Environmental Protection Agency, and by a National Science Foundation graduate fellowship.

STUDY OBJECTIVES: This paper demonstrates that EDB is transformed at low concentrations (25 to 90 µg/L) under similar methanogenic batch and continuous-flow column conditions.

RECOGNIZED METHOD: No. Comparable to OECD guideline 307, Aerobic and Anaerobic Transformation in Soil

GLP: Not stated.

TEST SUBSTANCE: Reagent grade EDB obtained from Matheson Chemical Co., Norwood, Ohio (purity not given). 1,2-dibromo[U-^{14}C]ethane (14.6 mCi/mmol) obtained from Amersham Corp., Arlington Heights, Illinois. Purity: Not given.

CONTROLS: Sterile batch controls were run concurrently.

EXPOSURE PERIOD: For the batch cultures, the sterile controls were exposed for 0, 1, 2, 4, 14, and 17 weeks. The seeded culture batches were exposed for 2, 4, 14, and 17 weeks.

EQUIPMENT: EDB was measured with a detection limit of 0.1 µg/Liter in water by using a pentane extraction, gas-chromatographic procedure with electron capture detection (1). Carbon-14 activity was determined by liquid scintillation counting with the channels ratio method for quench correction (2).

TEST PROCEDURE: Methanogenic batch suspended-growth experiments and a continuous-flow biofilm column study were performed to demonstrate EDB transformation. Sterile serum bottles containing deoxygenated medium for cultivating methanogens (3) were inoculated with EDB and a methanogenic mixed culture. These bottles were incubated in the dark at 35 degrees C and were periodically assayed for EDB and transformation products. A continuous-flow methanogenic column study was conducted for about 1 year with the same mixed bacterial culture inoculum. EDB and several other halogenated aliphatic organic compounds were applied simultaneously to the methanogenic biofilm column at concentrations ranging between 10 and 30 µg/liter. Details of these methods have been discussed by Bouwer and McCarty (4).

RESULTS: EDB was transformed to below the detection limit in methanogenic cultures within the first 2 weeks of incubation (Table 1). Characterization of the remaining radiotracer activity indicated the formation of a highly volatile, nonhalogenated fraction, substantially more volatile than EDB (such as bromoethanol).

Under sterile conditions EDB is transformed by an abiotic process; whereas, in the presence of active microorganisms it was more rapid indicating that a biological mechanism predominated. Mineralization of EDB to CO_2 was not observed. EDB appeared to be reduced to a highly volatile hydrocarbon, with the liberation of inorganic bromide. This result agrees with that of Castro and Belser (5), who showed a nearly complete conversion of EDB to ethylene and bromide by reductive dehalogenation in soil-water cultures.

Table 1. Transformation of EDB in methanogenic batch cultures

Sample type and sampling wk	EDB concn (μg/liter)	% of initial activity remaining[a]	% of radioactivity in samples		
			[^{14}C]EDB	^{14}C-volatile hydrocarbon	Unidentified fraction
Sterile control					
0	89 ± 9	100 ± 2	100 ± 2	0 ± 1	0 ± 1
1	90 ± 9	100 ± 2	100 ± 2	0 ± 1	0 ± 1
2	81 ± 8	100 ± 2	ND[b]	ND	ND
4	60 ± 6	89 ± 3	ND	ND	ND
14	<0.1	84 ± 3	ND	ND	ND
17	<0.1	78 ± 3	0 ± 1	64 ± 6	36 ± 4
Seeded culture					
2	<0.1	40 ± 2	0 ± 1	41 ± 4	59 ± 6
4	<0.1	23 ± 2	0 ± 1	27 ± 3	73 ± 7
14	<0.1	13 ± 2	0 ± 1	31 ± 3	69 ± 7
17	<0.1	9 ± 2	0 ± 1	19 ± 2	81 ± 82

[a]The initial tracer activity in sterile controls and seeded cultures was 2,570 ± 50 dpm/mL.
[b]ND, Not determined.

The authors suggest that transformation may be an important mechanism for the removal of EDB that is present at low concentrations in reducing environments, particularly methanogenesis. Biological and abiotic processes both play a role. The biological processes is the most significant.

DATA QUALITY: The report relies on data that was published elsewhere. This makes it extremely difficult to judge the quality of the study. The study affords a insight into the possible transformation of EDB at low concentration under methanogenic conditions.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [ ]
4. not assignable [x]

REASON: Documentation insufficient for assessment.

REFERENCES:

1. Henderson, J. El, G. R. Peyton, and W. H. Glaze. 1976. A convenient liquid-liquid extraction method for the determination of halomethanes in water at the parts-per-billion level, p. 105-112. *In* L. H. Keith (ed.), Identification and analysis of organic pollutants in water. Butterworth's, Stoneham, Massachusetts.
2. Bell, G. G., and F. N. Hayes. 1958. Liquid scintillation counting. Pergamon Press, Inc., Elmsford, New York.
3. Owen, W. F., D. C. Stuckey, J. B. Healy, Jr., L. Y. Young, and P. L. McCarty. 1979. Bioassay for monitoring biochemical methane potential and anaerobic toxicity. *Water Res.*, 13:485-492.
4. Bouwer, E. J., and P. L. McCarty. 1983. Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. *Appl. Environ. Microbiol.* 45:1286-1294.
5. Castro, C. E., and N. O. Belser. 1968. Biodehalogenation. Reductive dehalogenation of the biocides ethylene dibromide, 1,2-dibromon-3-chloropropane, and 2,3-dibromobutane in soil. *Environ. Sci. Technol.* 2:779-783.
6. Wade, R. S., and C. E. Castro. 1973. Oxidation of iron(II) porphyrins by alkyl halides. *J. Am. Chem. Soc.* 95:226-230.
7. Bouwer, E. J., and P. L. McCarty. 1983. Transformations of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. *Appl. Environ. Microbiol.* 45:1295-1299.

17. REPORT NUMBER: BD-11

STUDY TYPE: Structure-activity relationships approach

STUDY TITLE: Experiences with the Test Scheme under the Chemical Control Law of Japan: An Approach to Structure-Activity Correlations

AUTHORS: Masahiro Kawasaki

DATE of REPORT: Published in *Ecotoxicology and Environmental Safety*. 4, 444-454, 1980.

TESTING FACILITY: Not applicable.

STUDY NUMBER: Not applicable.

SPONSOR: Not applicable.

STUDY OBJECTIVES: Share experiences of using structure-activity relationships approach under the Chemical Control Law of Japan.

RECOGNIZED METHOD: No.

GLP: Not applicable.

TEST SUBSTANCE: Not applicable.

CONTROLS: Not applicable.

EXPOSURE PERIOD: Not applicable.

TEST PROCEDURE: There was no test procedure. Rather this is an examination of the structure activity of various classes of chemicals as they relate to biodegradation.

RESULTS: There are no specific results for EDB.

DATA QUALITY: This report was given at the 6th International Symposium IAES-SECOTOX in Muchen, Germany in 1979. The intent of the report was to give general overview of the consistencies and inconsistencies experienced in trying to apply the Japanese criteria that allows for structure-activity relationship in applying data from one compound to a new compound. As such, the data are not readily useful for evaluation purposes.

RELIABILITY:

1. w/o restriction [ ]
2. w restriction [ ]
3. not reliable [ ]
4. not assignable [x]

REASON: This is a theoretical paper that relies on data that are not available to the reviewer. The intent of the author was to assess structure-activity relationships as they can applied within the context of Japanese law.

REFERENCES: None.

18. REPORT NUMBER: BD-12

STUDY TYPE: Bioavailability of 1,2-dibromoethane

STUDY TITLE: Bioavailability of 1,2-Dibromoethane in fumigated soils

AUTHORS: Joseph J. Pignatello

DATE of REPORT: Published, "Preprint Extended Abstract" Presented before the Division of Environmental Chemistry, American Chemical Society, Denver, Colorado, April 1987.

TESTING FACILITY: The Connecticut Agricultural Experiment Station, 123 Huntington Street, New Haven, Connecticut.

STUDY NUMBER: Not given.

SPONSOR: Not given

STUDY OBJECTIVES: To test whether EDB was available for transformation by naturally occurring microorganism.

RECOGNIZED METHOD: No. OECD 307, Aerobic and Anaerobic Transformation in Soil.

GLP: Not stated.

TEST SUBSTANCE: ^{14}C-EDB;Purity: Not given.

EXPOSURE PERIOD: 24 - 38 days.

TEST PROCEDURE: Soil that was contaminated with EDB (<200 ppb) was suspended in water (1:1) and amended with ^{14}C-EDB. At specific times, replicates were taken for methanol extraction to recover total EDB, that was then analyzed by GC and liquid scintillation counting.

RESULTS: Comparison of native field residues to ^{14}C-EDB amended residues showed the amended resides were rapidly and nearly complete degraded. There was little or no degradation of the "native" field residue after 24 –38 days. The author notes that in other experiments ^{14}C-EDB was converted to $^{14}CO_2$ (about 45%) and unextractable ^{14}C associated with solids and taken to be cell material (about 55%).

One of these soils was further incubated with ^{14}C-EDB at 3 degrees C to reduce microbial degradation and allow greater time for ^{14}C-EDB to penetrate particles. Some sets of replicates were warmed to 25 degrees C to monitor ^{14}C-EDB degradation. 97% of the ^{14}C-EDB was degradable.

The author concludes from this that the native EDB in previously fumigated soils is inaccessible to microbes. Furthermore, EDB in this state does not exchange chemically with added ^{14}C-labelled EDB. Further evaluation of this native EDB demonstrated that it can be released following pulverization, but not via anionic and non-ionic surfactants, that had no effect upon its release. It was suggested that EDB from prior use had become entrapped in intraparticle micropore sites which is the reason for its persistence in topsoils.

DATA QUALITY: This was an overview of the work that J. J. Pignatello et.al which was published among the abstracts of the ACS, National Meeting 1987. Thus, it is an abstract of more extensive work conducted by this author. Practically all of the information was previously review as part of this robust summary paper.

RELIABILITY:

9. w/o restriction [ ]
10. w restriction [ ]
11. not reliable [x]
12. not assignable [ ]

REASON: The document is an abstract of a more thorough published paper.

REFERENCES:

1. Steinberg, S. M., J. J. Pignatello, and B. L. Sawhney. Submitted for publication, *Environ. Sci. Technol.* The paper is more than likely the following: Persistence of 1,2-Dibromoethane is soils: Entrapment in Intraparticle Micropores. *Environ.Sci. Technol.* Vol 21, No. 12, 1987 pp 1201-1208 (Report BD-9 in the robust summaries).

TABLE 2 –DATA MARTIX: ENVIRONMENTAL FATE AND ECOTOXICITY TESTS FOR: **ETHYLENE DIBROMIDE**

CAS #	CHEMICAL NAME	ENVIRONMENTAL FATE TESTS				ECOTOXICITY TESTS		
		Photodeg OECD 113	Stab.InWater OECD 111	Biodeg. OECD 301 302, 308	Tran/Dist. EQC MOD	Aquatic OECD 203	Invert. OECD 202	Plants OECD 201
106-93-4	ETHYLENE DIBROMIDE	**PH-1 (2)**	**HY-1(2)**	BD-1 (3)	MOD-1 (4)			
		PH-2 (4)	HY-2 (4)	**BD-2 (2)**	**MOD-2(2)**			
				BD-3(2)				
				BD-4(2)				
				BD-5 (2)				
				BD-6 (2)				
				BD-7 (4)				
				BD-8 (2)				
				BD-9 (4)				
				BD-10 (4)				
				BD-11 (3)				
				BD-12 (3)				

Studies in **BOLD** are critical studies. Klimisch ratings are in ( ).

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